RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XV NUMBER 4

October, 1942

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

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Vol. XV October, 1942 No. 4

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($2.50 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

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THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

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FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, BUFFALO, N. Y., SEPTEMBER 10-11, 1942

The annual fall meeting of the Division of Rubber Chemistry was held in Buffalo, N. Y., September 10-11, as a part of the 104th Meeting of the American Chemical Society. This meeting was one of the most successful in the twenty-three years since the formation of this Division in April, 1919.

Because of the unprecedented demands on the time and energy of all technical men in the rubber industry immediately following the beginning of the war, the Executive Committee had voted not to meet in Memphis last April with the rest of the Society. Partly as a result of this fact, and particularly as a result of the untiring efforts of the Chairman and active support of the membership—an unusually fine technical program was arranged. The principal theme in this program as well as that of the General Meeting of the Society, which preceded it on September 9, was synthetic rubber.

The attendance at the technical sessions, held in the Hotel Lafayette, headquarters of The Division, varied between 600 and 750. It is estimated that 500 to 600 were members of The Division, an exceptionally high proportion of the total membership was in attendance.

In opening the technical papers program, Chairman J. N. Street reviewed the difficulties which had been experienced in arranging the program as a result of the restrictions of wartime censorship and the steps which had been taken to insure that The Division meet all requirements in this respect. In spite of these precautions, one of the papers finally scheduled, "Improved Method of Reclaiming Rubber" by J. M. Bierer and W. W. Evans, had to be withdrawn at the last minute.

It was announced also that the Second Goodyear Lecture, which was to have been given by L. B. Sebrell, had been cancelled in the interest of war-time secrecy. This lecture would have dealt with synthetic rubber, and it may be scheduled for the next meeting of The Division if circumstances permit. A number of other papers dealing with synthetic rubber which were submitted, but were not released

for this meeting, are being carried on the active list for presentation at some future meeting.

The technical papers program follows:

Thursday Morning—Sept. 10.

1. Methylethyl Ketone Extraction of Rubber. LaVerne E. Cheyney.
2. The Effect of Temperature and Pressure on the Oxygen Pressure Test. Part I. A Comparison of Aging at 70° and 80° C. Part. II. The Effect of Oxygen Pressure on Aging at 80° C. A. M. Neal, H. G. Bimmerman and J. R. Vincent.
3. Growing Rubber in North America. H. L. Trumbull.
4. USF-Rubber. A New Crude Rubber. J. McGavack, C. E. Linscott and J. W. Haefele.
5. A Motion Picture Study of Balata and *Hevea* Latices, with Some Observations on Buna-S and Neoprene Latices. Francis F. Lucas.
6. The Natural Aging of Reclaimed Rubber. Henry F. Palmer and Robert H. Crossley.

Thursday Afternoon—Sept. 10.

7. Vibration Properties of Rubber. Dependence on Temperature. R. B. Stambaugh.
8. The Properties of Rubber Solutions and Gels. Maurice L. Huggins.
9. An x-Ray Study of Chemical Reactions Involving Accelerators in Rubber Compounding, and of Orientation of Crystalline Phases on Stretching of Various Stocks. G. L. Clark, R. L. LeTourneau and J. M. Ball.
10. Intermolecular Forces and Mechanical Behavior of High Polymers. H. Mark.
11. Significance of the Theory of Rubber Elasticity for the Development of Synthetic Rubbers. Hubert M. James and Eugene Guth.
12. Stress-Temperature Relations and Creep for Synthetic Rubbers. L. E. Peterson, R. L. Anthony and Eugene Guth.
13. Rise of Temperature on Fast Stretching of Synthetics and Natural Rubbers. S. L. Dart, R. L. Anthony and Eugene Guth.

Friday Morning—Sept. 11.

14. The Statistics of Cross-Linking Reactions in High Polymers. T. Alfrey, G. Goldfinger and H. Mark.
15. Molecular Weights and Intrinsic Viscosities of Polybutenes. Paul J. Flory.
16. The Action of Organic Accelerators in Buna-S. G. R. Vila.
17. The Effect of Different Carbon Blacks in Synthetic Tire Rubber Compounds. B. S. Garvey, Jr. and J. A. Freese, Jr.
18. Perbunan Properties and Compounding. R. A. Moll, R. M. Howlett and D. J. Buckley.
19. Butyl Rubber Properties and Compounding. J. P. Haworth and F. P. Baldwin.

Friday Afternoon—Sept. 11.

20. Ebonite from Hycar-OR. B. S. Garvey, Jr. and D. V. Sarbach.
21. The Evaluation of Small Amounts of Rubbers. B. S. Garvey, Jr.
22. The Processing Characteristics of Synthetic Tire Rubber and Their Evaluation. B. S. Garvey, Jr., M. H. Whitlock and J. A. Freese, Jr.
23. Unsaturation of Some Synthetic Rubberlike Materials. LaVerne E. Cheyney and Everett J. Kelley.
24. Thermal Decomposition of Natural and Synthetic Rubber Stocks. Irven B. Prettyman.

25. Density Measurements on Synthetic Rubbers. Lawrence A. Wood, Norman Bekkedahl and Frank L. Roth.

26. Low-Temperature Testing of Rubber. Influence of Variable Stress on Brittle Point. G. G. Winspear, F. S. Malm and A. R. Kemp.

27. Effect of Aniline Points of Oil on Swelling of Synthetic Rubbers. A. C. Hanson.

28. Effect of Petroleum Products on Neoprene Vulcanizates. III. Effect of Kerosenes. Donald F. Fraser.

29. Factors Influencing the Volume Change of Hycar-OR Compounds in Oil. A. E. Juve and B. S. Garvey, Jr.

The Society had planned for its General Meeting, a program of four papers which would review the progress of the rapidly expanding synthetic rubber development undertaken by the Government as a result of the war in the Pacific. However, two of these papers, "Progress on Synthetic Rubber Production" by E. R. Weidlein and "The Outlook on the Rubber Situation" by an unannounced author, were withdrawn by the Directors of the Society at the suggestion of the authors because it was felt that their presentation would be untimely in view of the pending Baruch report. The two papers presented were "Progress of Butadiene Production" by Albert L. Elder and "Progress of Styrene Production" by Willard Dow. Most of these papers, as well as most of those in the Divisional program dealing with synthetic rubber, will appear in the November issue of *Industrial and Engineering Chemistry,* and in a forthcoming number of this journal.

At the business meeting, the results of the election by letter ballot of officers for 1942-1943 were announced:

Chairman	John T. Blake
Vice-Chairman	Harold Gray
Secretary	H. I. Cramer
Treasurer	C. W. Christensen
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Directors	J. N. Street
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	A. W. Carpenter
	C. C. Davis
	S. G. Byam

The Chairman reported that the Treasurer's books had been audited by a committee headed by Enos Baker and found to be in order, and that the finances of The Division were in a satisfactory state.

A summary of the present status of the membership of The Division and of subscriptions to *Rubber Chemistry and Technology* was reported by C. R. Haynes, Chairman of the Membership Committee, as follows:

Total membership on August 31, 1942		974
Members paid for 1942	837	
Associate members paid for 1942	137	
Subscriptions to *Rubber Chemistry and Technology* (including 150 for Rubber Manufacturers' Association but excluding the 974 to general membership)		295
Honorary members and exchanges		16

The Chairman expressed his appreciation of the fine support given him during the past year by the officers and members of The Division and of the excellent work of Chairman John Plumb, Vice-Chairman Burt Wetherbee, and Secretary Howard Wiley, and their Committees in making all local arrangements for the meeting.

Chairman-elect J. T. Blake outlined plans of The Division for the coming year. Those for the 1943 meetings will depend on the progress of the war and on the decisions of the Society with respect to its national conventions. The Division has tentatively agreed to meet with the Society in Indianapolis in the Spring, but it is probable that the Fall Meeting will be held in Akron or some eastern city.

The Division Banquet, at the Hotel Statler, September 10, with 625 in attendance, was most successful. The local committee is to be commended for providing an excellent program and dinner without having to resort to donations, and without having to call on the treasury for more than two per cent of the surplus remaining from the Banquet at the Atlantic City Meeting. The Division is indebted to the Buffalo Rubber Group for its wholehearted assistance and coöperation in making the Buffalo Meeting so outstanding.

H. I. CRAMER, *Secretary.*

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1941. (VOL. 5). Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W.1, England. $7\frac{1}{4} \times 9\frac{1}{2}$ in. 145 pp. Price to Members: 2/6 (approximately 60c); Price to Non-Members: 10/6 (approximately $2.50).

This latest report on the progress of rubber technology covers developments in all fields and branches during 1941. Like previous editions, each subject is assigned to a prominent and recognized technologist or expert. The data are drawn from sources throughout the world, and each chapter has a bibliography. The subjects and their authors follow:

Historical and Statistical Review, T. R. Dawson; *Planting and Production of Raw Rubber and Latex, Gutta-Percha, Balata, Chicle and Jelutong,* T. R. Dawson; *Properties, Applications and Utilization of Latex,* C. F. Flint; *Chemistry and Physics of Raw Rubber and Rubber Derivatives,* W. J. S. Naunton; *Synthetic Rubber,* B. J. Habgood; *Testing Equipment and Specifications Other than for Latex,* W. J. S. Naunton; *Compounding Ingredients, Accelerators, Antioxidants and Softeners,* F. H. Cotton; *Fibres and Textiles,* W. Knight; *Chemical and Physical Properties of Vulcanized Rubber,* A. E. T. Neale.

Tires, H. Stanley; *Belting,* G. F. Payne; *Hose and Tubing,* J. Kirkwood; *Cables, and Electrical Insulation,* H. A. Daynes; *Footwear,* R. C. Davies; *Games, Sports Accessories, Toys,* J. P. Griffiths; *Mechanical Rubber Goods,* Herbert Rogers; *Roads,* G. E. Coombs; *Flooring,* J. Kirkwood; *Surgical Goods,* C. R. Pinnell; *Textile-Rubber Composites, Solvents, Cements,* W. N. Lister; *Sponge Rubber,* W. D. Guppy; *Hard Rubber,* B. L. Davies; *Works Processes, Materials, Including the Treatment of Raw Rubber in the Factory and the Treatment of Vulcanized Rubber,* F. H. Cotton; *Machinery and Appliances,* E. Morris.

Thanks are again due to T. J. Drakeley for the preparation of complete subject and author indexes. The Institution of the Rubber Industry is also to be complimented on its intention to publish these annual reports despite the difficulties raised by wartime conditions. [From *The Rubber Age* of New York.]

RUBBER. Smith, Barney & Co., 14 Wall St., New York, N. Y. 6 x 9 in. 24 pp.

This is an excellent survey of the current status of the rubber industry. It reviews consumption of rubber in recent years, discusses future requirements (based on Leon Henderson's recent figures), outlines stocks on hand and sources of supply, and explains the projected synthetic rubber program. In summing up the outlook for the rubber industry, the conclusion is drawn that "despite the

acute rubber shortage as far as the man in the street is concerned, the rubber industry is going to be fairly busy, apart from such armament orders as aeroplane assembly or machine-gun manufacture." The point is made that, as is usual under abnormal economic conditions, "certain companies are going to fare better than others, and some are going to be badly hit." An encouraging prediction is made to the effect that "the post-war rubber industry will handle a volume of business never achieved in prewar years." [From *The Rubber Age* of New York.]

RUBBER PRODUCING PLANTS, OTHER THAN GUAYULE AND RUBBER TREES. Library Bulletin 12. Prepared by Morris E. Paddick. Colorado State College Library, Fort Collins, Colo. 1942. 10 pages.

This bibliography for investigators of rubber-producing plants covers magazine articles, abstracts, and government publications in the United States and foreign countries. There are references to *kok-sagyz*, rabbit brush, milkweed, goldenrod, Colorado rubber plants, and other latex-bearing species. [From the *India Rubber World*.]

EXTRACTION OF RUBBER FROM PLANTS. Muriel E. Whalley. National Research Council of Canada, Ottawa, Canada. 8½ x 11 in. 19 pp. 25c.

This timely report on methods of extracting rubber from plants has been prepared as an aid to experiment work in this field. Some of the methods described are very old, many of them developed before world-wide use was made of the rubber plants in the East Indies, but nevertheless are valuable today. The report comprises three sections: (1) a section on methods in which the original articles have been reviewed in some detail; (2) a list of references; and (3) other material in abstract form of which complete articles were not readily available to the compiler. [From *The Rubber Age* of New York.]

PATENTS AND INDUSTRIAL PROGRESS. George E. Folk. Published by Harper & Brothers, 49 East 33rd St., New York City. 5½ x 8½ in. 393 pp. $3.00.

Coming as it does when the entire patent structure of the United States is facing complete overhauling as a result of an intensive investigation being made by a special committee of the Senate, this book should prove doubly welcome to manufacturers, inventors, designers, and others to whom the issuance of patents means profit or loss.

The book deals with the recent testimony presented before the Temporary National Economic Committee. During these hearings, voluminous testimony was presented, covering practically every phase of the patent system. This testimony is summarized, analyzed and evaluated by the author, who has had more than forty years of intimate experience with the American patent system. He is also special patent adviser to the National Association of Manufacturers.

The cases presented to TNEC by both the Department of Justice and the Department of Commerce, and the recommendations made by the investigating committee for legislation based on the proposals submitted by the government departments, are included. The book is divided into seven parts, includes a list of cases cited, and is complete to a subject index. [From *The Rubber Age* of New York.]

GUAYULE. General Tire & Rubber Co., Akron, Ohio, 5½ x 8½ in. 16 pp.

The story of guayule to date is very well told in this little booklet. The history of the plant since its discovery in Mexico some fifty years ago is given, with information on how and where guayule grows and how it yields its rubber. The

resin problem is reviewed as is the economics of cultivation and use. Both the McCallum five-year cycle plan and the Spence plan for broadcast sowing are discussed. The claim is made that, for tire use, guayule is superior to present-day synthetic rubbers. [From *The Rubber Age* of New York.]

ISOMERIZATION OF PURE HYDROCARBONS. Gustav Egloff, George Hulla, and V. I. Komarewsky. Published by Reinhold Publishing Co., 330 W. 42nd St., New York, N. Y. 1942. American Chemical Society Monograph Series. Cloth, 6 by 9¼ inches, 499 pages. Bibliography, author and subject indexes. Price $9.

This diversified study covers in detail and with critical acumen the results of many thousand experiments in structural, geometric, and optical isomerization of aliphatic, alicyclic, and aromatic compounds. An introductory chapter surveys the general background of this chemical phenomenon of fundamental molecular transformation, which is of invaluable scientific and commercial importance in the petroleum and other industries. Of increasing importance is the isomerization of alkanes, such as the conversion of butane into isobutane, followed by dehydrogenation to isobutene, a base material for polymerization in butyl rubber production. Many reactions from petroleum research, including those of butane, isobutane, butene, isobutene, and butadiene, are included.

Nearly half the volume consists of exhaustive tables of isomerization reaction data not elsewhere available in chemical literature. These should prove of inestimable assistance to research and other chemists. [From the *India Rubber World*.]

FACTICE. Abstracts of Articles and Patents. Muriel E. Whaley. National Research Council of Canada, Ottawa, Ont., Canada. 50 pages. Price 50c.

This compilation of abstracts of articles and patents concerning factice was made from the British Chemical Abstracts (1892-1940), American Chemical Abstracts (1907-1941), and from books. The abstracts are generous in content and competently done. The articles are arranged alphabetically according to author, and the patents are listed chronologically. [From the *India Rubber World*.]

THE SURFACE AREA OF COLLOIDAL CARBONS. Columbian Colloidal Carbons, Volume III. Columbian Carbon Co., Binney & Smith Co., Distributers, 41 E. 42nd St., New York, N. Y. 96 pages.

Part I. "Measurement by the Electron Microscope." Definitions of the various types of blacks in the "colloidal carbon spectrum" are given, and the previous work on particle size of Micronex black, reported in Volume II of this series, is reviewed and brought up to date, together with the results of similar work on other members of the colloidal carbon family. Spherical shape is shown to preponderate in all cases of the various types of blacks studied. The absence of elongated or acicular habit in the semireënforcing, lampblack, and acetylene carbons is stated as requiring a new theoretical approach to the problem of modulus and hardness. The rubber-compounding properties of the carbons therefore were considered as requiring review.

Part II. "The Role of Surface Area in Rubber Reënforcement". Results of work on "Rubber Compounding Properties", "Surface Chemistry and Behavior in Rubber", "Colloidal Properties and Surface Area", "Color, Strength and Oil Absorption *vs.* Surface Area", "Rubber Properties and Surface Area", and "Carbon Surface and Tread Quality" are reported in this second part of the booklet, which also includes a summary of the effects of the blacks on the rubber properties

tested and conclusions on "The Role of Surface and of Structure". A bibliography is also given. In the work on "Rubber Compounding Properties", a standard tread compound, Captax-accelerated, and loadings of 20 to 150 per cent by weight of the various blacks on the rubber was used for investigation of the properties of the various blacks in this natural rubber compound. Graphs show the variation of energy absorption, tensile strength, modulus at 300 per cent elongation, Shore hardness, rebound, plasticity, and electrical resistivity with different loadings of the different blacks, and the properties are discussed with relation to rubber processing and finished product quality. [From the *India Rubber World*.]

NATURAL AND SYNTHETIC HIGH POLYMERS. K. H. Meyer. Translated by L. E. R. Picken. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York, N. Y. 6 x 9 in. 690 pp. $11.00.

This book, the fourth volume in the High-Polymer Series being published by Interscience Publishers, is actually complementary to the second volume in the series: "The Physical Chemistry of High Polymeric Systems," by H. Mark. The two books are designed to replace a second edition of a short monograph published in German by the two authors about twelve years ago. Certain general lines in the field of high-polymer chemistry suggested in the earlier German work are extended in the present volume.

The book contains a great deal of theory on the highly individual behavior of high polymeric compounds. From this the author has proceeded from the standpoint that all those phenomena frequently regarded as peculiar to high polymers are to be referred, in a last analysis, to the interplay of atomic forces of attraction and thermal agitation, as in the behavior of compounds of low molecular weight. In many cases it was necessary for the author to put forth a theory where none existed before. Furthermore, as in the treatment of rubber, gutta-percha, and starch, it was necessary to undertake experimental work to obtain insight into obscure relationships. Since the results of these investigations are published for the first time, the volume is a doubly welcome addition to the technical literature.

Naturally, no discussion of natural or synthetic high polymers would be complete without a review of natural and synthetic rubbers. Accordingly, the author devotes approximately seventy-five pages to these materials in three separate sections: Rubber and Gutta-Percha, Physical Properties of Rubber, and Artificial or Synthetic Rubbers. These are included in the chapter on "High Polymeric Hydrocarbons and Their Derivatives". The literature is well reviewed and, as noted before, several new contributions based on personal work are included.

The book is divided into eleven chapters: The Study of High Polymers; Inorganic High Polymers; High-Polymeric Hydrocarbons and Their Derivatives; Polymeric Ethers, Esters, Sulfides, etc.; Cellulose and Its Derivatives; Substances Related to or Associated with Cellulose; Starch and Related Carbohydrates; Proteins; Properties of High Polymers in Solution; Films, Foils and Membranes; and Molecular Structure of Animal and Plant Tissues. In addition, there is an eight-page introduction, in which high polymers are defined and classified and the morphological approach to the chemistry of high polymers is discussed, as well as complete author and subject indexes. [From *The Rubber Age* of New York.]

STRATEGIC MATERIALS AND NATIONAL STRENGTH. Harry N. Holmes. The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1942. Cloth, 8¼ by 5½ inches, 106 pages. Index. Price $1.75.

This timely volume briefly discusses every sort of material needed for the war effort, stockpiles, sources of supplies, and shortages or abundances of each. How

other countries have met or tried to meet the problems of shortages of critical materials, and the ways in which the United States is trying through substitution and research to solve the same or similar problems are related.

How, at what cost, and to what extent the rubber shortage is likely to be alleviated by increased production of guayule and synthetics, and from available crude and scrap sources is realistically presented. Of rabbit brush growing wild in the Southwest, which an official government commission has reported would yield 125,000 tons of rubber, Dr. Holmes says:

"If we do nothing about it in the immediate future this resource will still be available later when the rubber shortage makes us willing to try anything."

The author is professor of chemistry in Oberlin College and 1942 president of the American Chemical Society. [From the *India Rubber World*.]

RUBBER-TIRED EQUIPMENT OF PRINCIPAL FARM MACHINES. A. P. Brodell and R. A. Pike. Issued by the Bureau of Agricultural Economics, Department of Agriculture, Washington, D. C. 8 x 10½ in. 8 pp.

This report summarizes information collected last year on the use of rubber tires on tractors and some other farm machines. The data was supplied by more than 25,000 crop correspondents who reported on machines for their locality, and on more than 17,000 tractors on their own farms. The reports provided complete information as to the age and type of the tractors and the extent of the use of rubber tires for more than 13,000 tractors. [From *The Rubber Age* of New York.]

RUBBER REQUIRED TO MAINTAIN USABLE PASSENGER CARS IN SERVICE. A Report of the Advisory Subcommittee on Rubber Economics to the Committee on Synthetic Rubber of the Petroleum Industry War Council. May 27, 1942. Petroleum Industry War Council, 700-B Shoreham Hotel, Washington, D. C. 13 pages.

Graphs, tables, and text of this report suggest that civilian automotive economy can be maintained, but at a reduced level, if small allotments of crude and reclaimed rubber are made available. [From the *India Rubber World*.]

STRUCTURE OF THE BUTADIENE-STYRENE COPOLYMER *

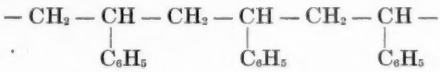
E. N. ALEKSEEVA and R. M. BELITZKAYA

POLYMERIZATION LABORATORY, KARPOV PHYSICOCHEMICAL LABORATORY, MOSCOW, U.S.S.R.

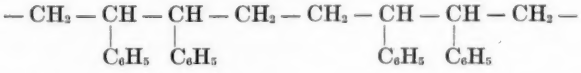
The joint polymerization of butadiene and styrene, like any other joint polymerization, can result either in a mixed polymer or in a copolymer. The macromolecules of the mixed polymer are the result of interlinkage of the monomeric units of one and the same kind, whereas the macromolecules of the copolymer are formed by alternation of the two structural (monomeric) units in the same macromolecule, following some definite pattern.

The most suitable method of solving the question proved to be, as in previous work (cf. Alekseeva, *Z. Obshcheĭ Khimii* **9**, 1426 (1939), ozonolysis, followed by oxidation of the decomposition products of the ozonides with dilute hydrogen peroxide, and separation of the mixture of the acids obtained through the medium of their methyl esters.

In case each monomeric component should polymerize individually, the styrene should yield a high molecular hydrocarbon with saturated carbon chain with phenyl groups acting as side chains:

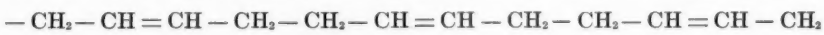


or

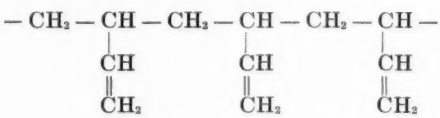


Such a hydrocarbon should be very stable towards ozone in low concentrations.

As for butadiene, its molecules can combine either in their 1,4-position, with formation of a high molecular unsaturated hydrocarbon with straight chain:



or else linkage can take place in the 1,2-position, with formation of a saturated main carbon chain with unsaturated side-chains:



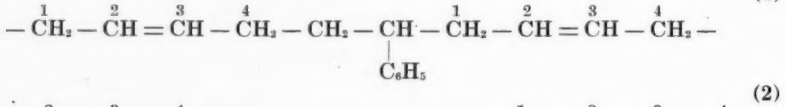
Finally both types of polymerization may occur in the same macromolecule, with formation of strongly branched macromolecules. In the first instance, ozonolysis should yield succinic acid; in the second instance, formic acid and a high molecular polycarboxylic acid; and, in the third instance, probably a rather high molecular polycarboxylic acid, with considerable side-chain formation.

If, on the other hand, we consider a copolymer to be the result of joint polymerization, the structure of its macromolecules will depend both on the law governing the alternation of the monomeric units, and on the method of

* Translated by Anselm Talalay for RUBBER CHEMISTRY AND TECHNOLOGY from the *Zhurnal Obshcheĭ Khimii*, U.S.S.R., Vol. 11, Part 4, pages 358-362 (1941).

linkage between the individual structural units. The possible types of linkage of the structural units are represented by the following schemes:

(1)



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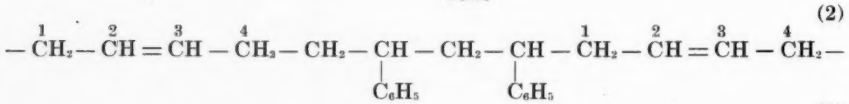

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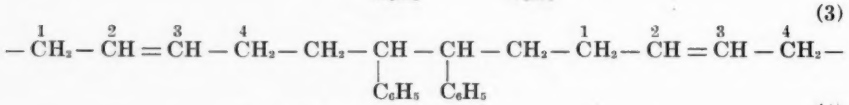

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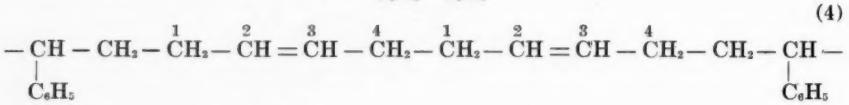

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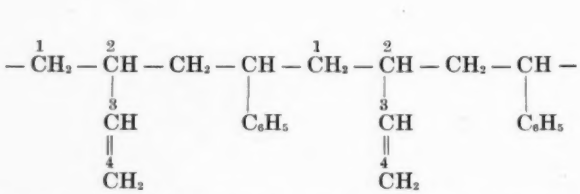
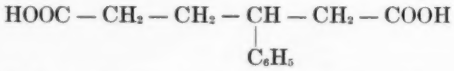
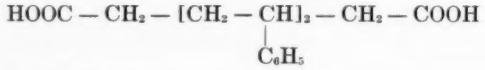


Finally a mixed type (6) could result, in which case the butadiene units are linked to the styrene units both in the 1,2- and the 1,4-positions.

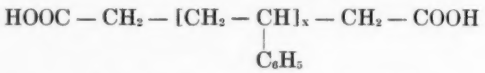
Ozonolysis, followed by oxidation with hydrogen peroxide, should lead to phenyladipic acid by scheme (1):



by schemes (2) and (3), to isomers of diphenylsuberic acid:



and if we assume that more than 2 molecules of styrene intercombine consecutively in a macromolecule, acids of the following type should result:



Scheme (4) should yield, in addition to the above acids, succinic acid, and schemes (5) and (6) should yield a mixture of formic acid and of high-molecular polycarboxylic acids.

Actually the following acids were isolated and identified: formic acid, succinic acid, phenyladipic acid, and diphenylsuberic acid. In addition, a number of high-molecular acids were obtained, which could not be identified. These acids were rich in carbon and had a low equivalent, indicating that they were formed as the result of mixed polymerization whereby the molecules of butadiene had combined both in the 1,2- and in the 1,4-positions.

EXPERIMENTAL PART

The polymer was obtained by joint polymerization of butadiene and styrene in the weight ratio 1:1 (*i.e.*, 2 molecules of butadiene for each molecule of styrene). The polymerization catalyst was benzoyl peroxide; 3 per cent based on the polymerization mixture was used. Polymerization required 210 hours at 60° C. The polymer obtained was freed of the admixed monomeric compounds first by evacuating to 2 mm. Hg, whereupon the polymer was ground and extracted with alcohol. The alcohol was removed under vacuum at 35-40° C.

The polymer thus freed of the monomers and alcohol was finely ground, and was placed for 3 days in small batches of 1.5-2.0 grams in 200 cc. of dry chloroform. It was then subjected to ozone treatment with a current of oxygen containing 1.5-2.0 per cent ozone. Ozonization was continued, with ice-cooling, until the polymer was completely dissolved; this required 5-6 hours. The chloroform was driven off under reduced pressure. The ozonides were decomposed by boiling with a 3 per cent solution of hydrogen peroxide. A part of the decomposition product went into aqueous solution; a part separated out in the form of a pale-yellow, waxy mass, soluble in alcohol. After cooling, the aqueous solution was decanted, and the water insoluble residue was washed with water. The wash-water was combined with the aqueous solution. The volatile components were separated by distilling the aqueous solution in vacuum at 30-40° C, and cooling the receiver with a mixture of snow and salt. The distillate was analyzed for aldehydes and formic acid. From the nonvolatile acids remaining after the water was driven off, succinic acid was isolated by fractional crystallization. The residue was a pale yellow syrupy mass.

The soluble was well as the water-insoluble acids were converted into their methyl esters by dissolving them in anhydrous methyl alcohol containing 5-6 per cent of dry hydrogen chloride. The solution was left cold for 24 hours, was then warmed for 1½ hours over a waterbath with a reflux condenser, and was treated in the usual manner. The mixture of the esters obtained was fractionated under vacuum.

As the result of the above treatment, 32 grams of the polymer yielded 3.22 grams of formic acid (HCOOH was determined by titration with alkali, and as a check by oxidation with potassium permanganate solution), 10.41 grams of crystalline succinic acid, 21.2 grams of water-soluble acids and 19 grams of water-insoluble acids.

Twenty grams of the water-soluble acid yielded 18.5 grams of methyl esters, which, on fractionation, resulted in the following fractions.

Fraction 1, at 85° and 2 mm. pressure	4.2 g.
Fraction 2, at 125° and 2 mm. pressure	5.2 g.
Fraction 3, at 140° and 0.05 mm. pressure	2.8 g.
Fraction 4, at 170-180° and 0.05 mm. pressure	3.5 g.
Residue	2.2 g.

Determination of the molecular weights of the ethers by the cryoscopic method:

Fraction 2: 0.1590 g. substance; 21.1 g. CH_3COOH; $\Delta t = 0.112°$.
0.3207 g. substance; 21.1 g. CH_3COOH; $\Delta t = 0.233°$.
Found: M 262, 254.4.
$C_{14}H_{18}O_4$, calculated M 250.

Fraction 3: 0.1700 g. substance; 17.8 g. CH_3COOH; $\Delta t = 0.152°$.
0.2501 g. substance; 17.8 g. CH_3COOH; $\Delta t = 0.228°$.
Found: M 245, 240.
$C_{13}H_{16}O_4$, calculated M 236.

Fraction 4: 0.2100 g. substance; 24.1 g. CH_3COOH; $\Delta t = 0.130°$.
0.2901 g. substance; 24.1 g. CH_3COOH; $\Delta t = 0.177°$.
Found: M 261.4, 265.7.
$C_{12}H_{16}O_5$, calculated M 252.

ANALYSIS OF THE ESTERS OF THE WATER-SOLUBLE ACIDS

Fraction 1: 0.1574 g. substance; 0.2836 g. CO_2; 0.0959 g. H_2O.
Found %: C 49.14; H 6.75.
$C_6H_{10}O_4$ calculated %: C 49.31; H 6.84.
Fraction 2: 0.1887 g. substance; 0.4671 g. CO_2; 0.1180 g. H_2O.
Found %: C 67.51; H 6.95.
$C_{14}H_{18}O_4$ Calculated %: C 67.20; H 7.25.
Fraction 3: 0.1456 g. substance; 0.3510 g. CO_2; 0.0919 g. H_2O.
Found %: C 65.75; H 6.73
$C_{13}H_{16}O_4$ Calculated %: C 66.10; H 6.80.
Fraction 4: 0.2001 g. substance; 0.4569 g. CO_2; 0.1143 g. H_2O.
Found %: C 62.25; H 6.71.
$C_{13}H_{16}O_5$ Calculated %: C 61.90; H 6.34.
Residue: 0.2204 g. substance; 0.5472 g. CO_2; 0.1369 g. H_2O.
Found %: C 67.72; H 6.90.

TABLE I

DETERMINATION OF THE EQUIVALENTS OF THE ESTERS BY SAPONIFICATION

Fraction	Substance g. (grams)	0.1*N* NaOH (cc.)	0.1*N* HCl (cc.)	Equivalent (found)	Equivalent (calculated)	Remarks
1	0.1460	50	30.09	73.32	73	Dimethyl ester of succinic acid
2	0.1564	37.13	24.41	123	125	Dimethyl ester of phenyladipic acid
3	0.1842	37.13	21.12	115	118	Monomethyl ester of phenyladipic acid
4	0.1830	37.13	22.13	122	126	Monomethyl ester of phenylhydroxyadipic acid
Residue.	0.2260	46.03 ml 0.5*N* NaOH	42.02 cc. 0.5*N* H_2SO_4	113		

Nineteen grams of insoluble acids gave 16.4 grams of methyl esters. These could not be distilled without decomposition, even in a high vacuum.

DETERMINATION OF EQUIVALENT (CARRIED OUT IN ETHER-ALCOHOL-WATER SOLUTION)

0.2322 g. substance: 33.72 cc. 0.5*N* NaOH; 30.79 cc. 0.5*N* H_2SO_4.
Equivalent found: 168.7; calculated: 170.
0.2100 g. substance: 20.3 g. CH_3COOH; $\Delta t = 0.114°$.
0.2550 g. substance: 20.3 g. CH_3COOH; $\Delta t = 0.136°$.
Found: M 360, 365.
$C_{21}H_{24}O_4$ Calculated: M 340.
0.1887 g. substance: 0.4800 g. CO_2; 0.1180 g. H_2O.
Found %: C 69.38; H 6.95.
$C_{21}H_{24}O_4$ Calculated %: C 74.11; H 7.06.

A comparison of the butadiene and styrene contents in the starting polymer and in the products isolated is given in Table II.

Thus, the quantity of the products obtained accounts for 88.45 per cent of the butadiene and 71.1 per cent of styrene in the starting polymer. Formic acid was formed as the result of mixed linkage of monomeric units, whereby the butadiene combined both in its 1,2- and its 1,4-positions Simultaneously

compounds should have been formed, with rather high molecular weights with considerably branched chains. It is to this type of compounds that the distillation residue of the methyl esters of the water-soluble acids evidently belongs, although in the present work, attempts to identify them were not successful.

TABLE II

Substance	Quantity of substance (grams)	Butadiene (grams)	Styrene (grams)
Polymer	32	16	16
Formic acid	3.32	3.74	..
Succinic acid	10.41	4.76	..
Dimethyl ester of succinic acid	4.2	1.56	..
Dimethyl ester of phenyladipic acid	5.2	1.12	2.28
Monomethyl ester of phenyladipic acid	2.8	0.64	1.24
Monomethyl ester of phenyloxyadipic acid	3.5	0.75	1.48
Monomethyl ester of diphenylsuberic acid	16.4	1.59	6.35
		14.15	11.35

CONCLUSIONS

The experimental data indicate that joint polymerization of styrene and butadiene results in copolymers of varied structure.

Of the styrene, 31.2 per cent forms, with the butadiene, macromolecules in which the two components alternate regularly, whereby the butadiene combines in its 1,4-position.

Forty per cent of the styrene forms macromolecules, in which two units of styrene interlink adjacently. Such "styrene pairs" are separated by one or more molecules of butadiene polymerizing in their 1,4-position.

The remaining 29 per cent of styrene evidently enters into the composition of branched macromolecules, formed as the result of butadiene linking both in the 1,2- and in the 1,4-positions.

Taking into consideration the fact that formic acid must have been formed from macromolecules, with butadiene linked in the 1,2-position, we can conclude that 23.3 per cent of the butadiene polymerized in its 1,2-position, and the rest in the 1,4-configuration.

STRUCTURE OF THE BUTADIENE-METHACRYLIC NITRILE COPOLYMER *

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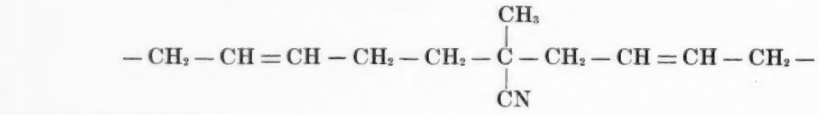
The technical literature contains numerous references to the method of joint polymerization in the synthesis of new types of rubber[1]. Comparatively few experimental data are, however, yet available to throw light on the structure of the macromolecules resulting from such simultaneous polymerizations. Ziegler[2] ascertained that vinyl compounds form, by joint polymerization with esters of acrylic acid, high polymeric substances whose macromolecules are composed of both (monomeric) components. Hill, Lewis and Simonsen[3] clarified the structure of the mixed polymer of butadiene with methyl methacrylate, and the present author[4] studied the structure of the copolymer of butadiene with acrylonitrile. The purpose of the present investigation is to clarify the molecular structure of the polymer resulting from the joint polymerization of butadiene and of the nitrile of methacrylic acid.

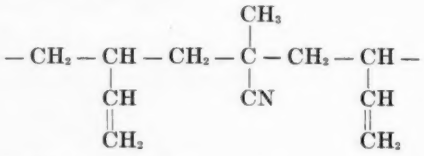
The method of ozonolysis was used in all cases to determine the structure of the macromolecules, since it makes possible the subdivision of the macromolecules into parts, maintaining intact the chain structure of the carbon skeleton of the original (polymeric) substance.

Several ways in which the macromolecules of the copolymer might have been formed are possible:

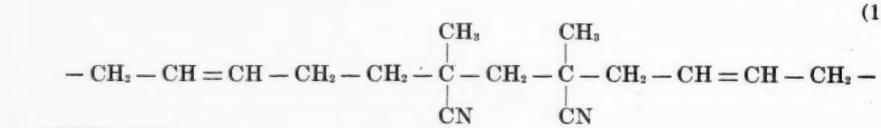
1. The two structural units regularly alternate in the macromolecule, whereby the butadiene polymerizes in the 1,4-position:



2. The two structural units regularly alternate in the macromolecule, but the butadiene polymerizes in its 1,2-position:



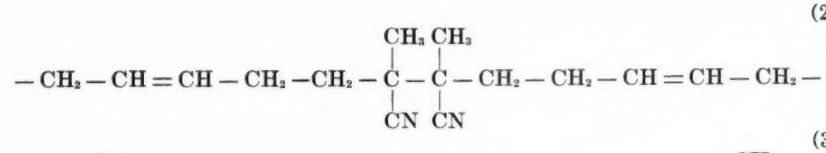
3. Two or more units of the same monomeric component intercombine:



(1)

* Translated by Leon Talalay for RUBBER CHEMISTRY AND TECHNOLOGY from the *Zhurnal Obshcheĭ Khimiĭ*, U.S.S.R., Vol. 11, No. 4, pages 353-357.

(2)



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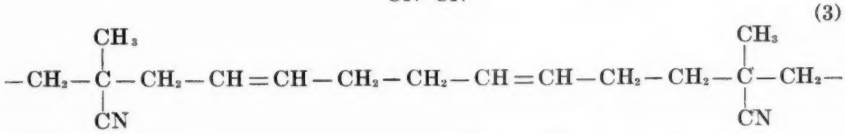

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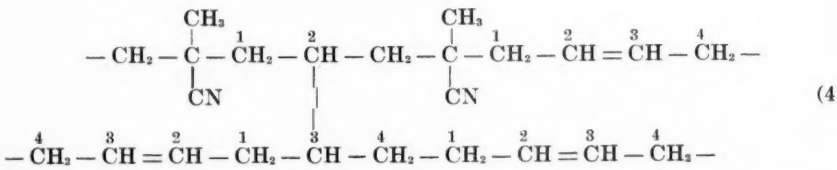
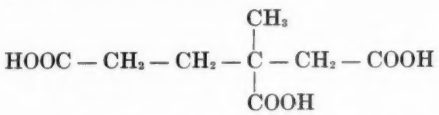
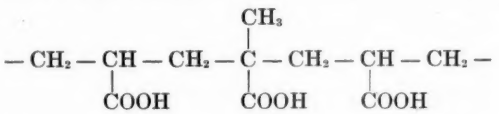


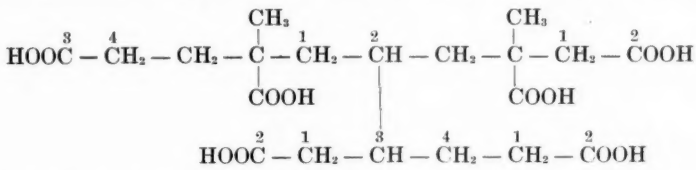
In the first case, ozonolysis, followed by oxidation with hydrogen peroxide, should yield 2-methyl-1,2,4-butanetricarboxylic acid.



In the second case, a high molecular polycarboxylic acid should be formed:



In the third case, one would expect the formation of dimethylhexanetetracarboxylic acid and of trimethyloctanetetracarboxylic acid of various structures, and of a high-molecular polycarboxylic acid with a branched carbon skeleton:



Actually, the main product isolated after ozonolysis of the butadiene-methacrylonitrile copolymer was found to be 2-methyl-1,2,4-butanetricarboxylic acid. The quantity of this compound corresponded to 62.2 per cent of the copolymer. In addition, 8 per cent of the copolymer was converted to succinic acid. On the basis of the above, one can arrive at the conclusion that, in the majority of the macromolecules of the copolymer, the two monomeric structural units alternate regularly; in this case polymerization of the butadiene takes place in the 1,4-position.

EXPERIMENTAL PART

The copolymer was obtained by joint polymerization of methacrylonitrile and butadiene in the molecular ratio 1:1 in the presence of 1 per cent of benzoyl peroxide for 98 hours at 60° C. The polymer was solid and pale yellow.

The shredded polymer was ozonized in ice-cold chloroform. Ozonolysis was carried out in small batches of 2 to 3 grams each. Twenty-four hours before the ozone treatment, a quantity of the polymer was weighed out, and was immersed in 200 cc. of dry, distilled chloroform. The polymer swells very strongly but does not dissolve.

Ozonolysis was effected by a current of oxygen, (containing 6-7 per cent ozone) at a rate of 400-450 cc. per minute. Treatment of each batch required 2 to 3 hours, and was continued until unreacted (unused) ozone turned the solution blue. During the ozone treatment the polymer gradually dissolves, and the ozonide partly settles to the bottom of the flask as a transparent viscous mass.

The chloroform was driven off under reduced pressure. The ozonide was boiled for 5-6 hours with 3 per cent hydrogen peroxide until it dissolved. In some instances 0.02 to 0.04 gram of a resinous residue remained after boiling.

The solutions obtained from the hydrogen peroxide treatment of the individual batches of the ozonides were combined. The water was driven off under reduced pressure at 30-40° C, leaving in the flask a pale yellow viscous mass, which was vacuum-dried (two to three mm. pressure) at room temperature.

Altogether 40.7 grams of the copolymer were subjected to ozone treatment.

Kjeldahl Analysis of the Copolymer

0.4266 g. substance: 19.34 cc. 0.5*N* H_2SO_4; 12.94 cc. 0.5*N* KOH
0.4269 g. substance: 19.34 cc. 0.5*N* H_2SO_4; 13.06 cc. 0.5*N* KOH
C_4H_5N content of the polymer: 50.20%, 49.27%

Weight of nitrile in the treated copolymer: 19.88 g.
Total insoluble residue after hydrogen peroxide treatment: 0.65 g.
Total acids formed: 60.8 g.

Kjeldahl Analysis of the Acids

0.4385 g. substance: 23.21 cc. 0.5*N* H_2SO_4; 18.80 cc. 0.5 KOH

To separate these acids, they were converted into their methyl esters.

For this purpose 33.6 grams of the acids were dissolved in 200 grams of anhydrous methanol containing 20 grams of hydrogen chloride. The solution was left 24 hours at room temperature and then warmed one hour over a water bath with a reflux condenser. The solution was cooled and the ammonium chloride filtered out. Two-thirds of the alcohol was driven off under reduced pressure, and the newly formed salts were again filtered off. In all 4.2 grams of ammonium chloride was separated.

The alcoholic solution of the complex esters, obtained after excess alcohol was driven off and the ammonium chloride filtered out, was diluted with five times its volume of water, whereby a pale yellow oil settled to the bottom. The mixture of alcohol and water was extracted several times with ethyl ether. The ether extracts were first washed with a 3 per cent solution of Soda, then with water and finally dried over calcium chloride. The ethyl ether was then driven off, and the mixture of complex esters was fractionated at 3 mm. Hg. The total quantity of complex esters, separated from the ethereal extract, amounted to 25 grams.

The distillation resulted in the following fractions:

Fraction I, 61°	5.5 g.
Fraction II, 70°	0.5 g.
Fraction III, 125-130°	12.5 g.
Fraction IV, 180°	3.5 g.
Fraction V, 215-220°	2.0 g.
Residue	1.0 g.

Fraction III was redistilled:

Subfraction 1, below 128°	0.5 g.
Subfraction 2, below 128°	3.5 g.
Subfraction 3, 136-142°	7.0 g.

The aqueous solution, obtained in the process of washing the ether extract, and containing dissolved complex esters, yielded 9.2 grams of a resinous substance contaminated with residual ammonium chloride.

This substance was completely dried in vacuum at 40° C. To separate it from the ammonium chloride, the vacuum-dried residue was repeatedly extracted with hot absolute alcohol. The alcohol was driven off under reduced pressure. In view of the fact, however, that ammonium chloride is somewhat soluble in hot absolute alcohol, the substance obtained was analyzed for its ammonium chloride content, and the quantity found was taken into account in the subsequent calculation of the results of analysis.

Determination of NH_4Cl in the Resinous Substance

(1) By titration with 0.1*N* $AgNO_3$ solution: 0.2300 g. substance; 5.07 cc. $AgNO_3$, therefore, total quantity of NH_4Cl in resinous substance—1.08 g.
(2) Ammonia distillation from alkaline solution: 0.5250 g. substance, 25.20 cc. 0.1*N* H_2SO_4 solution; 13.31 cc. 0.1*N* NaOH solution; total NH_4Cl content—1.09 g.

As may be seen from Tables I and II, analysis of the various fractions indicates the same 2-methyl-1,2,4-butanetricarboxylic acid (in the form of its neutral as well as of its acid esters) Somewhat less satisfactory are the results obtained for fraction V, corresponding to the monomethyl ester. This fraction, however, boils at 220° C (at 3 mm.), is distilled off from the residue and, therefore, is already subject to partial decomposition. Excess carbon content, compared with the theoretical, suggests that partial decarboxylation of the acid ester takes place during distillation.

A comparison of the butadiene and the nitrile content in the original copolymer, as well as in the products separated therefrom, is given in Table III. The products separated account for 78.8 per cent of the butadiene and for 69.7 per cent of the nitrile present at the start.

TABLE I

DETERMINATION OF THE EQUIVALENTS OF THE COMPLEX ESTERS OBTAINED BY SAPONIFICATION WITH 0.5*N* ALKALI

Fraction	Weight of specimen	cc. 0.5*N* KOH	cc. 0.5*N* H_2SO_4	Equivalent found	Equivalent calculated	Name of ester
I	0.3355	25	15.80	72.98	73	Dimethyl ester of succinic acid
II	0.2031	25	19.38	72.26	73	Same
IV	0.4231	29.32	18.26	76.5	77.3	Dimethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid
V	0.3200	25	16.36	74	72.66	Monomethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid
2	0.1857	29.85	25.35	82.54	82	Trimethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid
3	0.1884	23.88	19.34	83	82	Same
Residue from aqueous solution	0.5021 *	29.45	17.15	72	72.66	Monomethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid

* Specimen contained 0.0600 g. NH_4Cl.

TABLE II

ANALYSIS OF THE COMPLEX ESTERS

Fraction IV: 0.216 g. substance: 0.4121 g. CO_2; 0.1368 g. H_2O.
% found: C 51.95; H 7.02.
% calculated: C 51.72; H 6.89.

Fraction V: 0.1990 g. substance: 0.3709 g. CO_2; 0.1225 g. H_2O.
% found: C 50.81; H 7.40.
% calculated: C 49.54; H 6.42.

Fraction 2: 0.1593 g. substance: 0.3131 g. CO_2; 0.1053 g. H_2O.
% found: C 53.42; H 7.31.
% calculated: C 53.66; H 7.31.

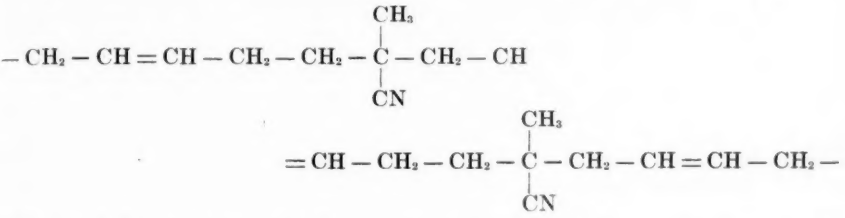
Fraction 3: 0.1684 g. substance: 0.3301 g. CO_2; 0.1320 g. H_2O.
% found: C 53.45; H 7.58.
% calculated: C 53.66; H 7.31.

TABLE III

Name of substance	Quantity of substance (grams)	Corresponding quantity of butadiene (grams)	Corresponding quantity of nitrile (grams)
Starting mixture of polycarboxylic acids.....	33.6	10.47	10.8
Dimethyl ester of succinic acid.....	6	2.22	...
Trimethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid	12.5	2.72	3.45
Dimethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid	3.5	0.81	1.0
Monomethyl ester of 2-methyl-1,2,4-butanetricarboxylic acid	10.1	2.48	3.03
		8.23	7.50

CONCLUSIONS

In the joint polymerization of butadiene and methacrylonitrile, the bulk of the polymer consists of macromolecules, in which the two unit components correctly alternate, and the butadiene combines in its 1,4-position.



Only much fewer macromolecules are encountered in which several molecules of butadiene consecutively intercombine in 1,4-positions.

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THE STEREOCHEMISTRY OF THE RUBBER MOLECULE *

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Rubber is usually amorphous at room temperature; the molecules are not arranged in a precise manner. But on cooling to about 0° C, it crystallizes. This transition is analogous to the melting or crystallization point of an ordinary small-molecule substance. It is true that the "melting point" of rubber is not sharp, and is variable in different specimens; moreover, below this socalled melting point, part of the substance remains uncrystallized, and, above the melting point, rubber is not fluid. But these are special modifying features, due to the long-chain character of the molecules; they do not alter the fact that the essential feature—the change of the bulk of the substance from a precisely ordered to a disordered state, or *vice versa*, at a fairly definite temperature—is analogous to the change: solid $\rightleftharpoons$ liquid, in a micromolecular substance.

In the attempt to understand the physical properties of rubber in terms of its molecular constitution, and in comparison with those of other long-chain polymers, the outstanding problem is that presented by its low melting point. The molecular weight of rubber is enormous, the number of carbon atoms in a molecule being on the average something like 10,000[1], yet the melting point of most specimens is no higher than that of a normal paraffin hydrocarbon containing only 14 or 15 carbon atoms.

For crystals composed of comparatively rigid molecules, the melting point depends in a general way on the molecular weight. It is reasonable to suppose that a crystal melts when the thermal vibrations of the molecules attain a certain amplitude. The amplitude attained at a given temperature depends on the weight of the molecule. But this is valid only for rigid molecules; for very flexible molecules the amplitude of thermal vibrations attained at any temperature depends on the weight of the sections of the molecule which may move relative to each other. This means that the melting point of a substance which is composed of very flexible molecules should be much lower than that of a substance which is composed of rigid molecules of the same weight. In crystals of long-chain polymers, the molecules are packed parallel, like a bundle of rods; the vibrations responsible for melting are almost exclusively vibrations perpendicular to the long molecules. The amplitude of lateral vibrations of sections of these chain molecules is likely to depend largely on the freedom of rotation around single chain-bonds, since the distortions arising in this way are likely to be far greater than those arising from the bending or stretching of the bonds.

If this is so, the differences between the melting points of different long-chain hydrocarbon polymers are to be ascribed to differences in the freedom of rotation around single bonds in the different molecules, and we are led to enquire why the freedom of rotation around single bonds is greater in rubber than in gutta-percha (the melting point of which is about 60° C) and much greater than in polyethylene (melting point about 115° C).

* Presented at a Discussion on "The Structure and Reactions of Rubber", held by The Faraday Society in London, May 29, 1942. Permission has been generously granted to publish this paper in RUBBER CHEMISTRY AND TECHNOLOGY.

I have suggested elsewhere[2] that the energy required for rotation around single bonds is made up of two factors:

(1) *The bond orientation energy.*—The bonds themselves prefer the staggered configuration (Figure 1); for rotation from one staggered position to the next, a definite energy is required.

(2) *The interaction of atoms or groups held by the bonds.*—Often this may be regarded as a geometrical effect; for instance, in diphenyl derivatives, the difficulty of rotation of the two rings (as shown by the temperatures of racemization of optically active substances) depends on the sizes of substituents in the 2, 2′, 6, and 6′ positions (I). Large substituents in these positions hinder rotation[3].

It is in relation to the second of these factors—the geometrical hindrance effect—that crystal structure determination is useful. For a chain polymer, it is necessary to know first of all the normal geometry of the chain and the positions of side-substituents. It will then be possible to consider what hindrances there are to rotation around the single bonds. Here, the structure of any one

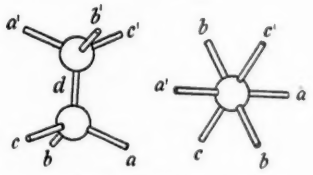
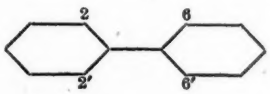


FIG. 1.—Preferred bond positions, Bonds staggered.



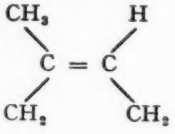
(I)

polymer is of little use by itself; but by determining the structures of a number of different molecules and comparing them, it is possible to draw some conclusions about the relative hindrances to rotation, and thus about the relative flexibilities of different molecules. In the case of rubber, comparison with its isomer, gutta-percha, is most informative.

The method of determination of the crystal structure of rubber by the interpretation of x-ray diffraction photographs of stretched specimens has been described elsewhere[4], and will not be repeated here. The accuracy with which the coördinates of the atoms in the unit cell may be determined is estimated to be, on the average, ± 0.05 A.U.; it may be rather less than this for some parameters and more for others.

The details of the packing of the molecules in the crystal need not concern us. The geometry of the molecule is displayed in Figure 2. The first point which emerges is that rubber is the *cis* form of polyisoprene, and gutta-percha (whose crystal structure was determined in the same investigation) is the *trans*-form. This is in accordance with expectation; it has been considered for some years that rubber is the *cis*-isomer, but proof was not forthcoming until now. The second feature of the molecular geometry which is significant from the present

point of view is the pronounced nonplanar character of the chain; the bonds attached to the double-bonded carbon atoms (II) lie roughly in a plane, but the



(II)

next chain-bond (the CH_2-CH_2 bond) lies away from this plane. The chain of gutta-percha is also nonplanar and is built on similar principles, except for the *trans* double-bond configuration. A third significant feature of the rubber

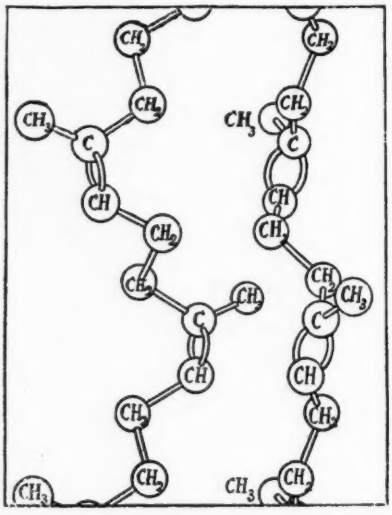


FIG. 2.—A rubber molecule, in the form it assumes in the crystal. Two views of the same molecule, from directions nearly at right angles to each other.

molecule is that the repeating unit of the chain molecule consists of two isoprene groups which geometrically differ considerably. An isolated molecule would have a two-fold screw axis of symmetry, but in the crystal this is not utilized, and alternate isoprene units are distorted in different ways. This difference is undoubtedly due to the mode of packing of the very awkwardly shaped molecules; the surroundings of one isoprene unit are different from those of the next unit in the chain. The fact that van der Waals' forces are able to cause such large distortions is testimony to the flexibility of the rubber molecule. Of particular interest is the evidence of considerable freedom of position of the bonds swivelling on the CH—CH_2 bond; this is brought out more clearly in Figure 3.

In one respect the crystal structure of rubber is less informative than that of gutta-percha, which gives clear evidence that, at the melting point, rotation around the single bonds occurs to an extent sufficient to convert a left-handed

to a right-handed molecule—a rotation of about 120°. It is reasonable to suppose that similar rotation occurs in rubber at its melting point, and I suggest that it is the sudden onset of this rotation of large amplitude which causes the melting of these substances.

If this is so, the melting point is determined largely by the amount of hindrance to this rotation. Of the two factors contributing to the energy of rotation—the bond orientation energy, and the geometrical hindrance factor—the first is likely to be the same in rubber as in gutta-percha, since the bond-sequence

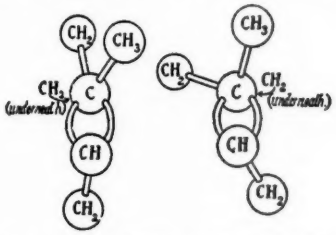


FIG. 3.—The difference between the two isoprene units forming the repeat period of the rubber molecule. Viewpoint—looking along the C—CH_2 bond.

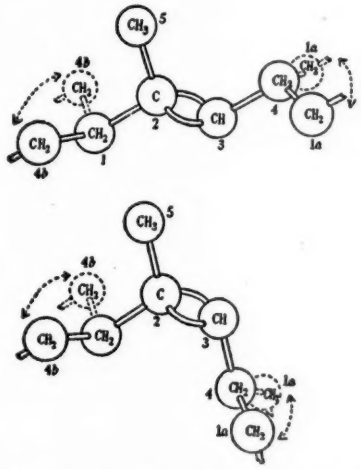


FIG. 4.—Bond-oscillation in gutta-percha (above) and rubber (below).

is the same in these molecules[2]. The second, the geometrical hindrance factor, is however, likely to be different in the two molecules, for reasons which are illustrated in Figure 4. When CH_2 group 4*b* swings around, as indicated by the arrow, the center of the carbon atom passes within 2.6 A.U. of the methyl group 5. Since the external radius of a CH_2 or CH_3 group is 1.8–2.05 A.U. (much greater than in the illustration), there will evidently be some hindrance to the rotation. All the atoms are vibrating, however, and at certain phases of the vibrations (when the methyl group 5 moves towards the right), 4*b* will be able to swing around, if the vibrations have sufficient amplitude. What has been said so far applies to either gutta-percha or rubber; where they differ is in the vibrations of the methyl group 5. In gutta-percha, vibrations of 5 towards the right are

restricted by group 4 (distance C4 to C5, only 3.0 A.), whereas in rubber no such obstruction is present. Therefore, in rubber, group 5 will be able to vibrate further towards the right than in gutta-percha, at any given temperature; the rotation of CH_2 group 4*b* may, therefore, occur at a lower temperature in rubber than in gutta-percha, and this, I suggest, is the reason for the lower melting-point of rubber.

The influence of geometrical factors on bond rotation and melting is shown still more clearly in the case of polychloroprene, the molecular structure of which is entirely analogous to that of gutta-percha, the chlorine atom taking the place of the methyl group. The chlorine atom stands further from the chain than the methyl group (C−Cl=1.77 A.U., C−C=1.53 A.U.), and is a little smaller than the methyl group; hence it offers less obstruction to rotation of the chain CH_2 group 4*b*; this is presumably the reason why the melting point of polychloroprene (about room temperature) is lower than that of gutta-percha.

The melting points of all these molecules containing double bonds are lower than that of polyethylene, which has a saturated chain. This may be due, partly, at any rate, to the fact that rotation around single bonds is easier when there is an adjacent double bond, as in the polyisoprenes than it is in a saturated molecule[5].

One of the most puzzling features in the behavior of rubber is the variability of its melting point. Most specimens of raw rubber have a melting point between −5° and +16° C[6]. But specimens kept in the crystalline condition at a low temperature for a long time melt at a higher temperature than 16° C; the highest melting point recorded is 41° C[7]. Specimens of smoked sheet rubber are sometimes partly crystalline at room temperature, and become completely amorphous only at 40° C. The question is, what is the true melting point of *cis*-polyisoprene? Is it −5° C or 41° C, or some temperature in between?

It is possible to suggest causes for either the raising or the lowering of the melting point. For instance, the high melting point of long-frozen specimens might be due to "setting" by cross-linking during the long freezing period. Similarly, processed specimens might be crystallized in certain regions by the strains set up in passing through rollers, and set in the strained (crystalline) condition by cross-linking. These are possible causes for the raising of the melting point. On the other hand, the presence of impurities in rubber hydrocarbon, either in the form of separate molecules or in the form of odd groups actually present here and there in the chains (interpolymerization), would be expected to lower the melting point. It does not appear possible to judge how far each of these factors modifies the melting point.

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MOLECULAR STRUCTURE AND RUBBER-LIKE ELASTICITY

I. THE CRYSTAL STRUCTURES OF β-GUTTA-PERCHA, RUBBER AND POLYCHLOROPRENE *

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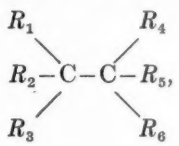
INTRODUCTION

The extraordinary mechanical properties of rubber, which have led to its widespread use for a variety of special purposes, seemed until recently very puzzling. Rubber did not appear to fit into any of the simple categories recognized by physical chemistry in the last century; in the ordinary condition at room temperature it is not a crystalline solid, nor a liquid; it could perhaps be classed with glasses as a noncrystalline solid, but its softness, flexibility and, above all, its enormous reversible extensibility, separate it widely from most other noncrystalline solids; its peculiar properties suggest a semiliquid nature; or perhaps it might be described as a viscous liquid with almost the coherence of a solid. Its mechanical properties are more like those of animal tissues than those of most laboratory chemicals, and the possibility that this similarity may not be entirely superficial lends additional interest to the search for an explanation of these mechanical properties in terms of molecular physics.

Within the last few years the possibility of arriving at such an explanation seems to have been brought nearer by the development of two concepts. The first is that rubber is a long-chain polymer. It was known that rubber is a polymer of isoprene, $CH_2=C(CH_3)-CH=CH_2$, and chemical evidence shows that the isoprene units are linked end to end (1:4)[1]. The viscosities of rubber solutions suggest strongly that the molecules are very long chains[2]. Chemically, raw rubber thus appears to be

$$(-CH_2-C(CH_3)=CH-CH_2-CH_2-C(CH_3)=CH-CH_2-)_n.$$

The second concept is that such long-chain molecules are likely to be very flexible. When two carbon atoms are joined together by a single bond:



the left-hand group can usually rotate with respect to the right-hand group around the central connecting link as axis. Such rotation around each of the single bonds of a long-chain molecule would obviously give rise to great flexibility; the molecule could easily assume an enormous number of different geometrical forms. It is natural to suppose that the flexibility of rubber is in some way due to the flexibility of the molecules themselves. Thus Mack[3] pic-

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tures the molecules in ordinary rubber as being closely coiled, whereas Mark[4], Kuhn[5], and Guth[6] suppose them to have a quite irregular configuration; the stretching of rubber is thought to be due to the straightening out of the molecules.

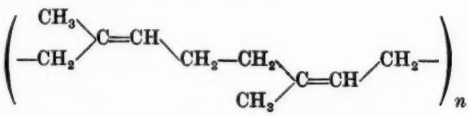
Not all long-chain polymers have rubberlike properties at room temperature, however. Consider, for instance, the properties of gutta-percha. This substance is, like rubber, a 1:4 chain-polymer of isoprene[7], yet its properties at room temperature are quite different from those of rubber; it is a crystalline solid, tough and hornlike in character. Thus, there are two substances, both chain polymers of the same monomer, which have quite different mechanical properties at room temperature. It is true that the average length of gutta-percha molecules (about 3000 carbon atoms) is apparently only about one-third that of raw rubber molecules (about 10,000 carbon atoms); but the difference in their mechanical properties is not solely or even mainly due to the difference in the lengths of the molecules, since rubber degraded to about the same molecular length as gutta-percha is still rubberlike and noncrystalline. If rubberlike properties are due to molecular flexibility, it appears that gutta-percha molecules are not flexible at room temperature; the supposition being that there is some geometrical difference between rubber and gutta-percha molecules, such that the latter have not the flexibility of the former.

Rubber in the ordinary condition at room temperature is amorphous, but Katz[8] discovered that it becomes crystalline on stretching to several times its original length. When a stretched specimen is released, the rapid contraction is accompanied by the disappearance of the crystalline structure and a return to the amorphous condition. The extraordinary mechanical properties of the substance are thus paralleled by the equally extraordinary behavior of its molecules, which actually arrange themselves in a precise pattern during stretching, and disarrange themselves on release. It is natural to suspect a vital connection between the two sets of phenomena, and to suppose that if it were known why the molecules were able to arrange and disarrange themselves in response to mere mechanical changes, it might then also be understood why the substance was elastic. The geometrical structure of the molecules themselves, and perhaps the nature of the arrangement of them in the crystal, should suggest some reason for such remarkable behavior.

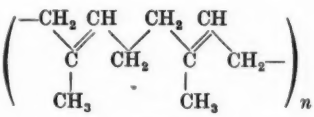
The x-ray diffraction photographs of crystalline rubber and gutta-percha show at once that the molecules are geometrically different. When rubber is stretched, it is natural to suppose that the long molecules become parallel to the direction of stretching, and the identity period of the crystals along the direction of stretching is, therefore, the identity period of the molecules themselves; this identity period is 8.1 A.U.[9]. Gutta-percha, already crystalline at room temperature, cannot be stretched reversibly to this extent, but it can be drawn out or rolled out irreversibly* so that all the crystals become parallel to the direction of drawing or rolling. Assuming that the long molecules are parallel to the direction of drawing or rolling, the identity period of the crystals along this direction is the identity period of the molecules. There are two crystalline forms of gutta-percha, known as α and β, and their identity periods in the direction of drawing are 8.9 and 4.7 A.U., respectively[10]. It appears, therefore, that there are two different chain forms of gutta-percha, both different from that of rubber. An obvious possibility of isomerism in 1:4 polymers of isoprene arises from the presence of double bonds in the chain, and it has been sug-

* The process becomes reversible at a temperature just below the melting-point.

gested[11] that rubber is the *cis* form, with chain bonds on the same side of the double bond, and that gutta-percha is the *trans* form, with chain bonds on opposite sides of the double bond[12]:



cis



trans

If this is true, the question arises as to why is the *cis* form of chain more flexible than the *trans* form? To answer this question, it is necessary to know more about the precise geometry of the molecules.

The position is complicated by the existence of two forms of gutta-percha. These two forms, which can be easily converted into each other but not into rubber, are evidently stereoisomers having different chain forms; if both have the *trans* double-bond configuration, they must differ in single-bond configuration.

Another substance whose molecular geometry appears to be of crucial importance is polychloroprene, the synthetic rubberlike substance which is the basis of Neoprene synthetic rubbers. Chemically, that is a 1:4 polymer, and differs from rubber and gutta-percha in having chlorine atoms in place of substituent methyl groups[13]:

$$(—CH_2—CCl=CH—CH_2—CH_2—CCl=CH—CH_2—)_n$$

The remarkable thing about this substance is that its identity period (4.79 A.U.) is almost exactly the same as that of β-gutta-percha (4.72 A.U.), suggesting the same chain structure, yet its mechanical properties at room temperature are like those of rubber, not those of gutta-percha. If rubberlike properties are due to molecular flexibility, why does the substitution of chlorine atoms in place of methyl groups increase the flexibility of the molecules?

The answers to such questions are presumably to be found in the geometry of the molecules. The first part of the present work has therefore been the elucidation of the crystal structures of the three substances mentioned—rubber, gutta-percha and polychloroprene. The β form of gutta-percha was studied first, as it appeared to offer the greatest chances of success; its identity period (4.7 A.U.) is shorter than that of rubber (8.1 A.U.), indicating a simpler chain structure, and it gives more detailed x-ray photographs than polychloroprene.

β-GUTTA-PERCHA

The Two Crystalline Forms of Gutta-Percha

The crystalline form which occurs in the tree is known as the α form. When heated above 65° C it becomes transparent, optically isotropic, and amorphous, giving an x-ray diffraction pattern of diffuse rings. If this amorphous material is cooled very slowly (0.5° C per hour) the α form recrystallizes, but if cooling is rapid, the β form crystallizes. The latter, on heating, becomes amorphous at 56° C. Thus the β form, since it has the lower crystallization point and is the first to crystallize on rapid cooling, is, strictly speaking, the less stable of the two at all temperatures; however, it appears to be permanently metastable at room temperature[10].

The x-ray diffraction photographs of the α and β forms are quite different, and the identity periods of drawn or rolled specimens of the two forms are different. Evidently this is a case of stereoisomerism, not one of the frequent examples of two different packings of the same molecules; the chain forms of the molecules are different. The two types of molecules are easily interconvertible, but neither of the forms can be converted into rubber.

Chain Form of β Molecules

The identity period of β-gutta-percha (4.7 A.U.) is so short that it is probable from the start that there is only one isoprene unit in this length. Of the *cis* and *trans* forms of molecule, only the latter is likely to have an identity period with one isoprene unit in it. A *trans* chain structure with all the carbon atoms in the same plane (Figure 1*c*, *d*) has been suggested for β-gutta-percha[12]. But accepting Robertson's interatomic distances[14] (C—C 1.54 A.U., C=C 1.33 A.U.)

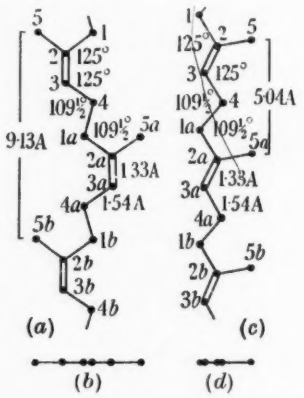


Fig. 1.—Planar polyisoprene models. (*a*) *Cis* chain. (*b*) End view of (*a*). (*c*) *Trans* chain. (*d*) End view of (*c*).

and the theoretical bond angles (>C 109½°, >C 125°), and assuming that the $\diagup CH_2 \diagdown CH_2 \diagup$ group forms a plane zigzag as in the long-chain normal paraffins[15], a planar *trans* chain (Figure 1*c*, *d*) would have an identity period of 5.04 A.U., a figure considerably in excess of the actual period of β molecules (4.7 A.U.). The only way of attaining the correct identity period without serious and improbable alterations of the interatomic distances and bond angles is to assume a nonplanar chain structure. Now, in ethylene[16] and its chlorosubstitution products[17], all the atoms in the grouping $\begin{matrix} a \\ b \end{matrix}\!\!\rangle C{=}C \langle\!\!\begin{matrix} c \\ d \end{matrix}$ are in the same plane. It is expected, therefore, that atoms 1, 2, 3 and 4 of the chain (Figure 1*c*), as well as the methyl carbon 5, will all be in the same plane. Each isoprene unit is thus expected to be planar, as far as its carbon atoms are concerned. The only way of attaining the correct identity period of 4.7 A.U., while keeping each isoprene unit planar, is to move bond 4–1*a* out of the plane 12345 by rotation round bond 3–4; at the same time, to keep isoprene unit 1*a*2*a*3*a*4*a*5*a* strictly parallel to isoprene unit 12345 so that the two remain crystallographically

equivalent, it is necessary to rotate bond 1*a*–4 around bond 1*a*–2*a*. Thus one isoprene unit has been moved towards the other along the chain axis while maintaining the correct distance between atoms 4 and 1*a* and maintaining the angles 341*a* and 41*a*2*a* at 109½°. There are two ways of doing this; bond 4–1*a* can be rotated either clockwise or anticlockwise; two different types of asymmetric molecule, each the mirror image of the other, are obtained in this way; they are shown in Figure 2. The end-views of such molecules show the four chain carbon atoms of each isoprene unit at the corners of a parallelogram. If each isoprene unit is planar, these are the only possible *trans* chain structures having a one-unit period of 4.7 A.U.

Crystal Structure Determination

x-Ray diffraction photographs of a piece of cold-rolled sheet were taken on a cylindrical camera with Cu $K\alpha$ radiation. Rolling has the advantage over drawing that it produces a double orientation effect; not only does the *c* axis of each crystal become nearly parallel to the direction of rolling, but also the *a* axis tends to lie in the plane of the sheet; this lateral orientation is far less perfect than the longitudinal orientation, but is useful for the purpose of checking the indices of the diffraction spots. In addition to the usual fibre photographs (with specimen vertical), another photograph was taken with the specimen horizontal and oscillating from a position normal to the x-ray beam to a position 45° to the beam; this photograph recorded the diffracted beams from the crystal plane perpendicular to the chain axis (the *c* axis). Similar oscillation photographs of rubber and polychloroprene specimens were subsequently taken during the work on those substances.

All the diffracted beams fit an orthorhombic cell containing four isoprene units. The photographs agree with those of Fuller[12] and the electron diffraction photographs of Storks[18], except in one particular; Fuller records some weak spots which appear to demand a larger cell; since these were not found even in dense photographs (and are absent from Storks's photographs), they must have been due to impurities in Fuller's specimens.

The *c* projection, giving an end-view of the molecules, was considered first. The problem was simplified by an apparent halving of the *b* axis from this viewpoint, a feature shown later to be an accidental pseudosymmetry, not a significant halving due to space group symmetry. It was found that no arrangement of planar molecules satisfies the (visually estimated) *hk*0 intensities; the only atomic positions which are satisfactory indicate a nonplanar molecule, whose end-view agrees approximately with that anticipated in Figure 2.

The space group was considered next. The possibilities are limited by the following consideration. β-Gutta-percha is made by cooling amorphous (melted) material rapidly. Melted gutta-percha is not a liquid but a somewhat rubber-like solid, hence the molecules do not move about relative to each other to any great extent (if they did, the material would be fluid). Neither can these enormously long molecules turn round to reverse their ends. Hence, on crystallization, the molecules settle down in an orderly manner while remaining more or less where they happen to be. There are evidently bundles of roughly parallel molecules in the amorphous material; all that happens during crystallization is that the molecules arrange themselves precisely, without moving about bodily to any great extent. Since in any bundle of molecules there are likely to be approximately equal numbers of up and down molecules (an up molecule being defined as one with the methyl group above the double bond, and a down mole-

cule the reverse), it is probable that each crystal contains equal numbers of up and down molecules; thus, of the four molecules passing through the unit cell, two are likely to be up and two down. Accepting this conclusion, and accepting also the approximate molecular positions found in the preliminary calculations of $hk0$ intensities, only three space groups are possible: $P\ 2_12_12_1$, $P\ 2_12_12$, and Pca (the last with axes interchanged $abc \rightarrow cab$). $P\ 2_12_12$ is ruled out by the absence of odd orders of $00l$. The final choice of space group was made, and atomic positions (for carbon atoms) found, by consideration of the

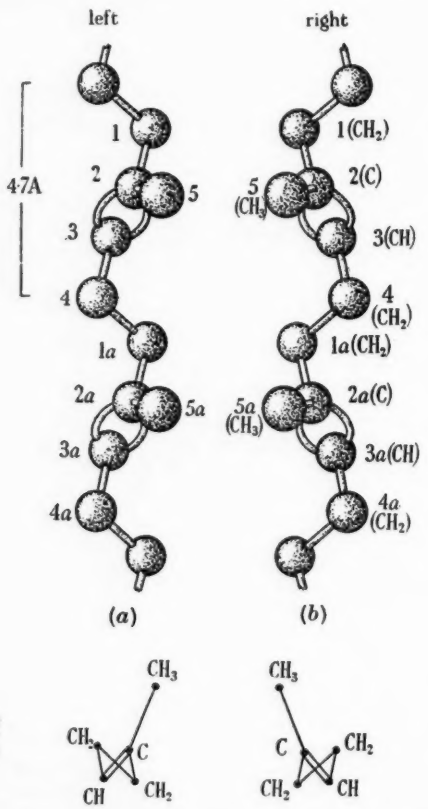


FIG. 2.—Molecular models assuming planar isoprene units (*trans*) and identity period of 4.7 A. Left- and right-handed molecules.

intensities of all the diffraction spots on the photographs. A fairly good agreement between observed and calculated intensities was obtained for the $P\ 2_12_12_1$ arrangement[19]. The calculations were much shortened by using charts of the type devised by Bragg and Lipson[30]. The method of using these for hkl intensities is described in an appendix.

DESCRIPTION OF CRYSTAL STRUCTURE

The unit cell is orthorhombic, with $a_0=7.78$, $b_0=11.78$, and $c_0=4.72$ A.U. Four long-chain molecules pass through this cell parallel to the c axis. The

space group is $P\ 2_12_12_1$, and the coördinates xyz of the carbon atoms of one right-handed down molecule (right-handed is defined in Figure 2) are the following:

C_1	$0.926a$	C_2	$0.000a$	C_3	$0.000a$	C_4	$0.074a$	C_5	$0.970a$	x
(CH_2)	$0.110b$	(C)	$0.146b$	(CH)	$0.074b$	(CH_2)	$0.110b$	(CH_3)	$0.277b$	y
	$0.676c$		$0.960c$		$0.177c$		$0.462c$		$0.980c$	z

The atoms of the other three molecules in the unit cell are at the other equivalent positions of space group $P\ 2_12_12_1$, i.e.

$$\tfrac{1}{2}-x,\ -y,\ \tfrac{1}{2}+z;\quad \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ -z;\quad -x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z.$$

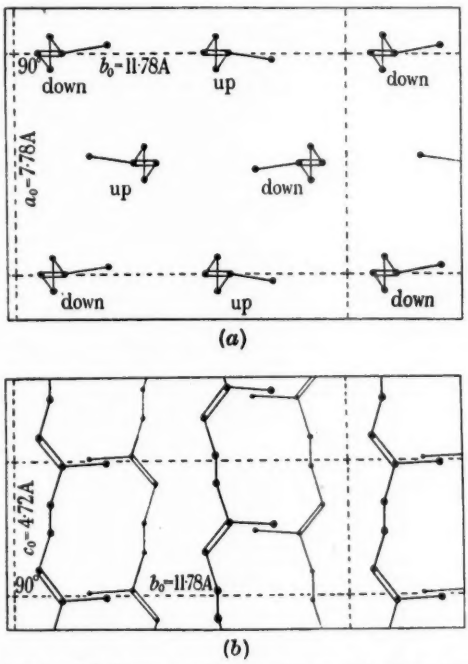


FIG. 3.—Structure of right-handed β-gutta-percha crystal, seen (*a*) along *c* axis, (*b*) along *a* axis.

All four molecules in the unit cell are identical—all right-handed in the example given here and illustrated by Figure 3 *a*, *b*; the crystal may be referred to as a right-handed crystal. Presumably, in any specimen, there are equal proportions of left- and right-handed crystals. The fact that in any one crystal all the molecules are either left-handed or right-handed, not mixed, attains some importance in the discussion of the origin of elasticity (Part III of this work).

The structure of individual molecules differs very little from the structure predicted in Figure 2. The chain-carbon atoms of each isoprene unit lie in a plane; atoms 1 and 4 are on opposite sides of the double bond, the chain thus being the *trans* form. All interatomic distances and bond angles in the chain are normal[20]:

$$\text{C}-\text{C}\ 1.54\ \text{A},\ \text{C}=\text{C}\ 1.33\ \text{A},\ >\text{C}\ 109\tfrac{1}{2}°,\ \geqslant\text{C}\ 125°.$$

The more noteworthy features of the molecular structure are illustrated more clearly in Figure 4. The most important feature is the nonplanar character of the chain; bond 1–4*b*, if it were in plane 1234, would lie along the broken line in the diagram; actually it makes an angle of 63° with this line; bond 4–1*a* is at the same angle on the opposite side of plane 1234. (Expressed otherwise, plane 4*b*–1–2 makes an angle of 115° with plane 1234.) The reason for this nonplanar character is discussed, in connection with the stereochemistry of other aliphatic molecules, in Part II of this work.

The position of the methyl group needs comment. The carbon atom of this group (5) is not in plane 1234; it is displaced 0.65 A.U. away from its ideal position in plane 1234. The main cause of this distortion is evidently repulsion of the chain CH_2 group 4*b* (Figure 4). The effective radius of a CH_2 or CH_3 group is 1.80–2.05 A.U. (depending on the direction—these groups are not spherical), and in all structures so far determined, the distance between such groups in neighboring molecules is 3.6–4.1 A.U. The distance between 4*b*

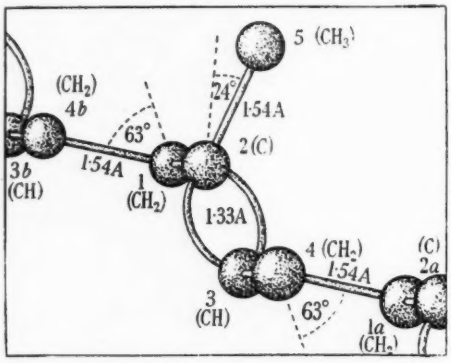


FIG. 4.—Details of structure of left-handed β-gutta-percha molecule. Distances 1-2 and 3-4 = 1.54 A.U. Angles 4*b*-1-2 and 3-4-1*a* = 109½°. Broken straight lines are in the plane 1234.

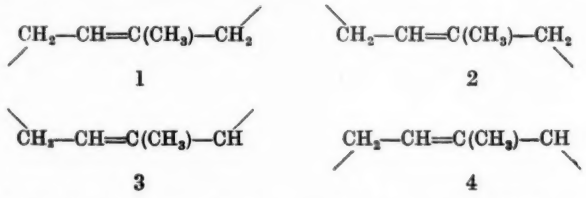
(a CH_2 group) and 5 (the CH_3 group), even in their present positions is only 3.2 A.U.; if the methyl group were in its ideal position in plane 1234, the distance would be still smaller. The reason for the distortion is thus obvious, but it remains surprising that it is so large. The determined position, however, must be accepted; although no great accuracy can be claimed, yet it seems quite impossible to account for the x-ray intensities except by assuming that the CH_3 group is in the position already given (within ±0.1 A.U. along *a*). Distortions of similar magnitude are found in the structure of rubber; and here it appears that intermolecular forces may also cause distortions (see below).

PROBABLE STRUCTURE OF α-GUTTA-PERCHA MOLECULES

Knowledge of the structure of β-gutta-percha appears to provide the key to the molecular structures of α-gutta-percha and of rubber, for, assuming bond orientations as in β-gutta-percha, it is possible to construct chains having the correct identity periods for the other two substances.

The α form of gutta-percha presumably has a *trans* double-bond configuration like the β form, but differently oriented connecting links between the *trans* isoprene units. The reason for the nonplanar character of the β chain will be

discussed later, in Part II; here it will merely be assumed that the CH_2-CH_2 chain bonds in other molecules make the same angle with the plane of the isoprene unit as in β-gutta-percha molecules. Four different orientations of the two connecting links of any one isoprene unit are possible; they can be represented (as well as is possible on a flat surface) thus:



The plane of the isoprene unit is supposed to be perpendicular to the plane of the paper, and the connecting links nearly in the plane of the paper. The methyl groups are supposed to be above the plane of the paper.

If a large number of units of type 1 are joined together, a left-handed β-gutta-percha molecule (Figure 2*a*) is obtained; if units of type 2 are used, a right-handed β molecule (Figure 2*b*) is the result. Units of type 3 alone, or 4 alone, give complex spiral molecules with very long periods, but if 3 and 4 are joined together alternately, a molecule with a two-unit period of 8.9 A.U. is obtained (Figure 5*a*). 8.9 A.U. is exactly the known identity period of α-gutta-percha; hence Figure 5*a* probably represents the structure of α molecules.

There is one other type of molecule with a two-unit period, obtained by joining types 1 and 2 together alternately (Figure 5*b*). The identity period of this molecule, which is thus a third possible form (γ) of gutta-percha, is 9.4 A.U., but so far such a form has not been encountered. Other combinations of the above four types of units give more complex molecules with very long periods, but these also have not been encountered, the only known forms of gutta-percha being the two already considered. (The tendency in nature is, of course, towards simplicity wherever possible.)

RUBBER

Possible Cis Chain Forms

Since gutta-percha has the *trans* double-bond configuration, rubber is presumably the *cis* form. The identity period of rubber molecules in a crystal is 8.1 A.U. A *cis* chain with all the carbon atoms in the same plane (Figure 1 *a, b*) would have an identity period of 9.13 A.U., assuming the normal interatomic distances and bond angles. Therefore it is to be expected that the carbon chain in rubber molecules is nonplanar. Each isoprene chain unit is expected to be substantially planar, hence likely nonplanar chain forms can only be constructed by placing the CH_2-CH_2 connecting links out of the planes of the isoprene units. It is reasonable to suppose that the angles between the connecting links and the planes of the isoprene units would be similar to those in gutta-percha molecules. It has been seen that there are four different arrangements of the pair of connecting links of each isoprene unit. Many different chain forms could be constructed by using these arrangements in different combinations, but it is found that there is no *cis* model with a one-unit period, and only two possible types with two-unit periods. One of these (Figure 5*c*), a molecule with a period of about 8.0 A.U., is constructed exclusively of units of type 3 (left-handed molecule),

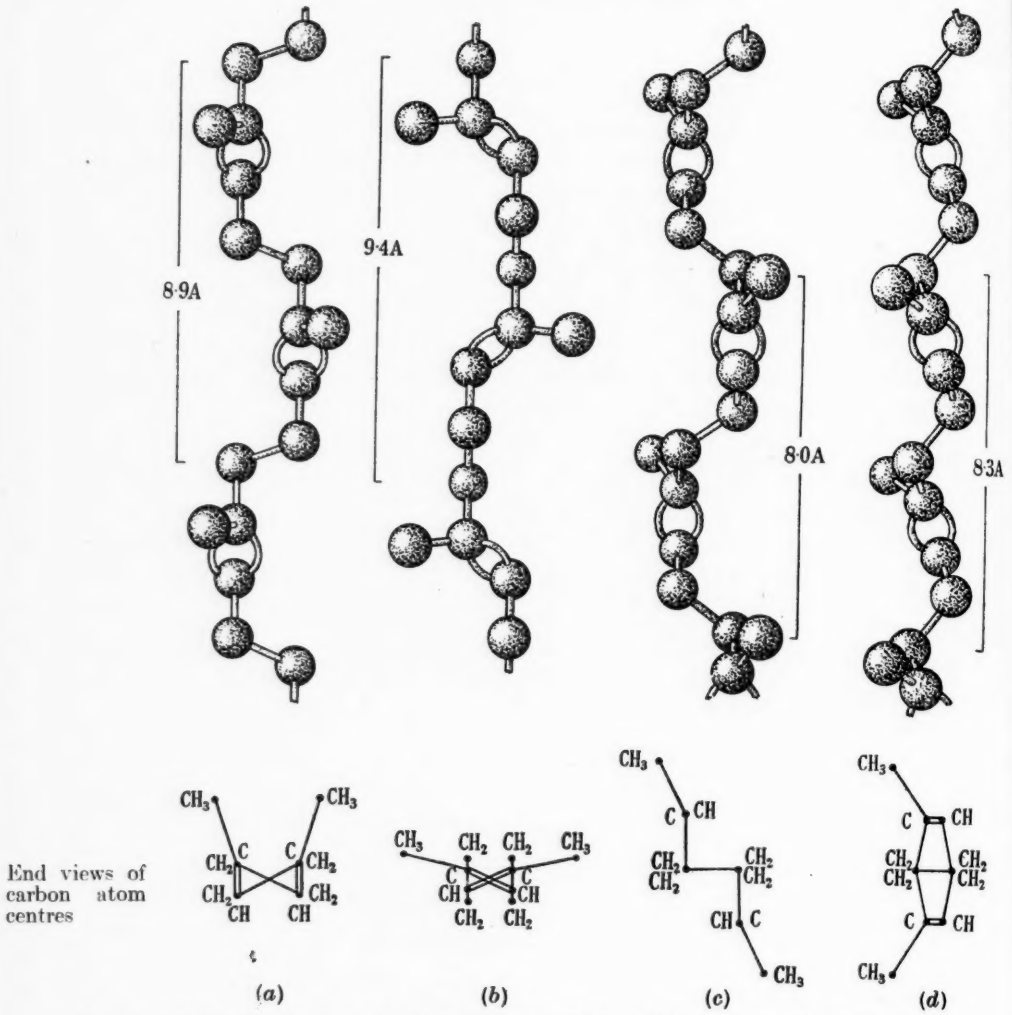


FIG. 5.—(*a*) Probable structure of gutta-percha. (*b*) Third possible form of gutta-percha (unknown), (*c*) and (*d*) *Cis* chains constructed according to the same principles of single-bond orientation.

or exclusively of type 4 (right-handed molecule). The other (Figure 5*d*), which has a period of about 8.3 A.U., is constructed of alternate units of types 1 and 2. Since neither of these periods agrees exactly with the known period of rubber, it does not appear possible to decide which model is correct; further, it appears that certain angles in the *cis* (rubber) chain are not quite the same as those in the *trans* (gutta-percha) chain. Nevertheless, the position is simplified by the above considerations to the extent that only two chain types need be considered.

DETERMINATION OF CRYSTAL STRUCTURE

Rubber may be caused to crystallize either by stretching a specimen to several times its original length, whereby crystals with one axis parallel to the direc-

tion of stretching are produced, or (usually) by cooling below 0° C, when crystals with random orientation are formed. The correspondence between the x-ray diffraction patterns of stretched and frozen specimens shows that the crystal structure, (*i.e.*, the molecular structure and the arrangement of the molecules, is the same in both types[21]. On account of the complexity of the structure, only oriented specimens can be used for structure determination. x-Ray diffraction patterns of stretched threads were first taken; these patterns correspond closely with those obtained by Morss[22] and Sauter[23]. In addition, a very marked double orientation effect was obtained by stretching thin sheets[24]; diffraction patterns from these sheets provided valuable information on the orientation of the crystal planes responsible for the different spots, and thus made it possible to check the indices.

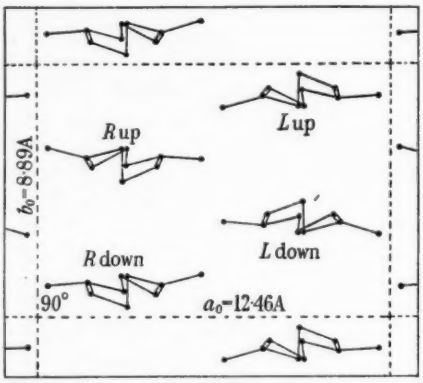
Several different unit cells have been suggested to account for the x-ray diffraction patterns of stretched rubber. Mark and Susich[9] and Sauter[23] suggested orthorhombic four-molecule (eight isoprene unit) cells of different dimensions; Lotmar and Meyer[25] proposed a monoclinic four-molecule cell. Morss[22] concluded that all the diffraction spots, except one very weak one, fit a four-molecule orthorhombic cell with sides $a_0=12.5$, $b_0=8.9$, and $c_0=8.1$ A.U. better than any other; this conclusion has been confirmed by the present work, and the intensities of spots from doubly oriented specimens confirm the indices assigned on this basis. Morss[22] suggested that the additional very weak spot demands an eight-molecule cell which might be either orthorhombic or monoclinic; actually this is not the only way of accounting for the extra spot, as we shall see later. It was decided to put aside this question and accept provisionally Morss's four-molecule orthorhombic cell for preliminary work on the structure.

There are very few equatorial spots on the fibre diagrams and, as Morss pointed out, the absences indicate that, seen along the fibre axis (the *c* axis), all the molecules look alike and form an arrangement which can be referred to a one-molecule projected pseudocell. This very much simplifies the problem. The two molecular models (or rather their end-on projections as shown at the bottom of Figure 5 *c*, *d*) were tried in turn in this one-molecule pseudocell; it was found that correct intensities for the diffractions from *hk*0 planes (the equatorial spots) cannot be obtained with model 5*d*, but that approximately correct intensities can be obtained with model 5*c*; the latter is accordingly indicated as the correct structure of rubber molecules. (For the arrangement of the molecules in the *ab* projection, see Figure 6*a*.)

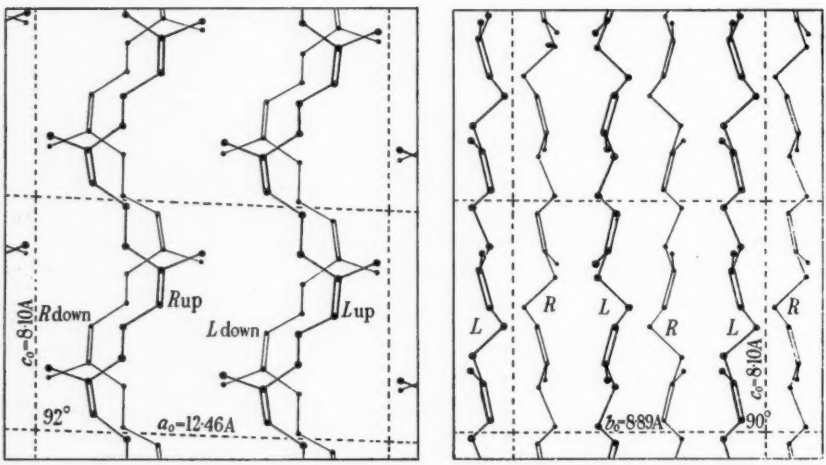
The *h*0*l* intensities were considered next; here, the absence of diffracted beams from planes with *h* odd indicates an apparent halving of the *a* axis for this viewpoint; thus, only two molecules have to be considered. The approximate atomic positions along *a* were already known. For reasons similar to those already given in the case of gutta-percha, there are likely to be equal numbers of up and down molecules in the crystal; hence, of the two molecules just mentioned, one is upside down with respect to the other (see Figure 6*b*). Relative positions of the two molecules giving approximately correct *h*0*l* intensities were easily found.

It was then necessary to consider the space group and the question of the extra spot which does not fit the four-molecule orthorhombic cell. The extra spot could be accounted for either by a four-molecule monoclinic cell, or by an eight-molecule cell which might be either orthorhombic or monoclinic. The former possibility was naturally considered first. The extra spot, which is rather

diffuse, is on the second layer line, and its spacing is nearest to that of $\bar{4}02$ and 322 of the provisional cell; by making the angle between the a and c axes 92° instead of 90°, the extra spot can be indexed as $\bar{4}02+\bar{3}22$ of a monoclinic cell; and the rest of the spots on the photographs also fit this cell within the limits of error of measurement. In this four-molecule monoclinic cell, the



(a)



(b) (c)

FIG. 6.—Crystal structure of rubber. (*a*) Seen along *c* axis. (*b*) Seen along *b* axis. (*c*) Seen along *a* axis.

only likely arrangement, in view of the absent reflections and the already known approximate molecular positions, is $P\ 2_1/a$. Atomic positions in $P\ 2_1/a$, giving approximately correct relative intensities for all the diffraction spots on the photographs, were finally found. It was found necessary to admit considerable distortions of the ideal model (Figure 5*c*) to obtain correct intensities.

DESCRIPTION OF CRYSTAL STRUCTURE

The unit cell is monoclinic with $a_0=12.46$, $b_0=8.89$, $c_0=8.10$ A.U., $\beta=92°$. Four long-chain molecules pass through this cell parallel to the c axis. The space

group is $P\ 2_1/a$; there are two left-handed molecules (one up and one down) and two right-handed molecules (one up and one down). The coördinates xyz of the carbon atoms of one left-handed up molecule are the following:

C_1	0.753a	C_2	0.854a	C_3	0.845a	C_4	0.745a	C_5	0.968a	x
(CH_2)	0.899b	(C)	0.865b	(CH)	0.905b	(CH_2)	0.959b	(CH_3)	0.876b	y
	0.802c		0.703c		0.542c		0.457c		0.773c	z
C_6	0.744a	C_7	0.644a	C_8	0.659a	C_9	0.757a	C_{10}	0.532a	x
(CH_2)	0.834b	(C)	0.874b	(CH)	0.905b	(CH_2)	0.834b	(CH_3)	0.828b	y
	0.326c		0.215c		0.052c		0.975c		0.268c	z

The atoms of the other three molecules are at the other equivalent positions of space group $P\ 2_1/a$:

$$-x, -y, -z;\quad \tfrac{1}{2}-x, \tfrac{1}{2}+y, -z;\quad \tfrac{1}{2}+x, \tfrac{1}{2}-y;\quad z.$$

The complete structure is illustrated in Figure 6 *a*, *b* and *c*. Details of the structure of one molecule are shown in Figure 7.

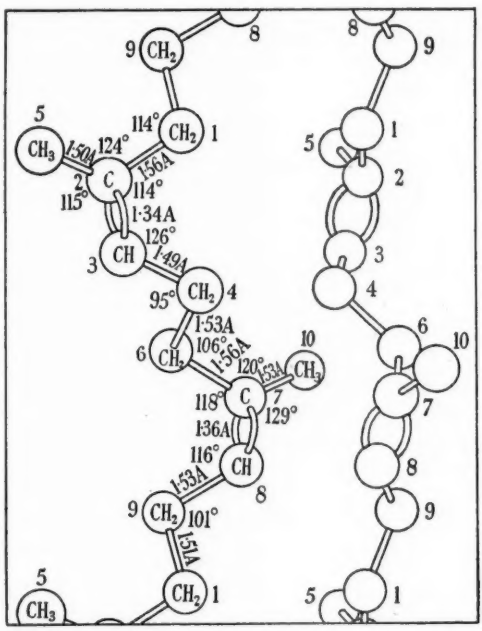


Fig. 7.—Left-handed rubber molecule, seen from two different viewpoints.

The atomic positions recorded above give approximately correct intensities for all the x-ray diffraction spots; but, in view of the complexity of the structure (in which there are 30 parameters), and the limited information obtainable from fibre photographs, the accuracy is naturally inferior to that obtainable in structure determinations based on single crystal photographs. For this reason, the atomic positions given here must be regarded as approximate only. The same applies to the other structures given in this work, but in a lesser degree on account of the comparative simplicity of the structures of β-gutta-percha and polychloroprene, in which there are only 15 parameters.

The geometry of the rubber molecule, as it exists in the crystal (Figure 7), shows considerable deviations from the ideal model of Figure 5*c*. In the first place, the two isoprene units which make up the identity period of an individual molecule are not identical in configuration. (This fact is revealed directly by the occurrence of a faint 001 diffraction spot, which was not seen by Morss[22], but was definitely obtained by Sauter[23] and in the present work.) Secondly, the double-bond chain units $C-C=C-C$ are not quite planar. Thirdly, the angles between the two CH_2-CH_2 chain bonds (C_9-C_1 and C_4-C_6) and the $CH_2-C=CH$ planes are different from each other and from the corresponding angles in β-gutta-percha. Also the methyl groups lie considerably off the $CH_2-C=CH$ planes, although this feature was anticipated through knowledge of the β-gutta-percha structure. The explanation of the last-mentioned feature is, no doubt, similar to that given in the case of β-gutta-percha—it is due mainly to repulsion between the CH_3 groups and particular CH_2 chain groups. The other distortions appear to be due to the packing together of very awkwardly shaped molecules; each molecule is distorted from its ideal form to pack better with its neighbors. Inspection of a model of the structure shows that all the distortions are reasonably explained (qualitatively) on this basis. This conclusion, that all the distortions which have to be admitted to account for the intensities of the x-ray diffraction spots, are exactly those to be expected on account of packing difficulties, gives confidence that the whole structure is substantially correct, though individual atomic positions may be rather approximate.

There is one other x-ray diffraction effect of rubber crystals which should perhaps be mentioned. Diffraction spots at very small angles, indicating spacings of 54 and 108 A.U., have been reported[26]. These spacings are many times greater than the unit-cell dimensions, and suggest some kind of superlattice. It seems possible that these spots, like the extra spots of aluminum, sodium chloride and magnesium oxide crystals investigated by Preston[27], are due to thermal vibrations in the lattice. Atomic and molecular vibrations are very slow compared with the frequencies of x-rays; consequently, with regard to x-rays, the atoms in the lattice are in effect at rest but displaced from their normal positions, some being displaced in one direction and others in other directions, according to the wave pattern in the lattice. A superlattice effect is thus produced by the thermal wave pattern in the lattice.

POLYCHLOROPRENE

Chain Form

It has already been remarked that the identity period of stretched polychloroprene (4.79 A.U.) is almost identical with that of β-gutta-percha (4.72 A.U.), and therefore it probably has the same chain structure, that is to say, it has a *trans* double-bond configuration and the same single-bond configuration as β-gutta-percha.

Crystal Structure Determination

Polychloroprene, like rubber, is usually noncrystalline at room temperature[28]; on stretching, oriented crystals are formed, and on release the molecules disarrange themselves again and the material again becomes noncrystalline. x-Ray diffraction photographs of stretched specimens were taken under similar conditions to those of β-gutta-percha and rubber. Compared with those of rubber,

the photographs have a higher background intensity; also the spots are longer arcs, showing that the orientation of the crystals is less perfect.

All the diffraction spots fit a four-molecule orthorhombic cell whose a axis is longer and whose b axis is shorter than those of β-gutta-percha. The $hk0$ intensities (those of the equatorial spots on the normal fibre photograph) were considered first; it was found possible to account for these only by the arrangement shown in Figure 8*a*, which is analogous to that of β-gutta-percha, although the orientation of the molecules is considerably different. In view of this arrangement, the space group of the whole structure is evidently $P\ 2_12_12_1$, if we accept the arguments advanced in the case of β-gutta-percha. The c ordinates of the atoms were found by consideration of the intensities of remaining spots; the data for this purpose are rather scanty, and therefore the positions of the atoms along the c axis are known with less accuracy than in the case of β-gutta-percha.

Description of Crystal Structure

The unit cell is orthorhombic, with $a_0=8.84$, $b_0=10.24$, $c_0=4.79$ A.U. Four long-chain molecules pass through this cell parallel to the c axis. The space group is $P\ 2_12_12_1$ (the whole structure being completely analogous to that of β-gutta-percha), and the coördinates xyz of the carbon and chlorine atoms of one right-handed up molecule are the following:

C_1	$0.077a$	C_2	$0.033a$	C_3	$0.008a$	C_4	$0.970a$	Cl	$0.167a$	x
(CH_2)	$0.054b$	(C)	$0.115b$	(CH)	$0.034b$	(CH_2)	$0.099b$		$0.243b$	y
	$0.278c$		$0.000c$		$0.787c$		$0.509c$		$0.000c$	z

The atoms of the other three molecules of the unit cell are at the other equivalent positions of $P\ 2_12_12_1$ (see β-gutta-percha structure). The complete structure is illustrated in Figure 8 *a, b;* the similarity to that of β-gutta-percha will be evident from these diagrams. All four molecules in the cell are identical—either all right-handed (in the example given here) or all left-handed, not mixed. Presumably there are equal proportions of left- and right-handed crystals in any specimen of stretched polychloroprene.

All interatomic distances and bond angles are normal. The distance C−Cl is 1.77 A.U., which is a little greater than the distance in CCl_4 (1.75 A.U.) and in chlorinated ethylenes (1.67–1.73) determined by electron diffraction in gases[29]. The double-bond unit C−C=C−C is very nearly planar, and the CH_2-CH_2-C plane is at about 120° to the $CH_2-C=CH$ plane (compared with 115° in β-gutta-percha). The C−Cl bond is not in the $CH_2-C=CH$ plane, but is displaced by an amount (40°) even greater than the displacement of the CH_3 group in β-gutta-percha (24°). This displacement is no doubt due, partly at any rate, to repulsion between the chlorine atom and chain CH_2 group C_4. Other influences, which may account for the larger angle in polychloroprene, are distortion of the molecules by others packed around them (as in rubber) and interaction of C−Cl dipoles in adjacent molecules.

The remarkable nonplanar chain forms of the molecules studied in this paper will be discussed in relation to the stereochemistry of aliphatic molecules in general in Part II, and the bearing of the results on the question of molecular flexibility and the molecular basis of rubberlike properties in Part III of this work.

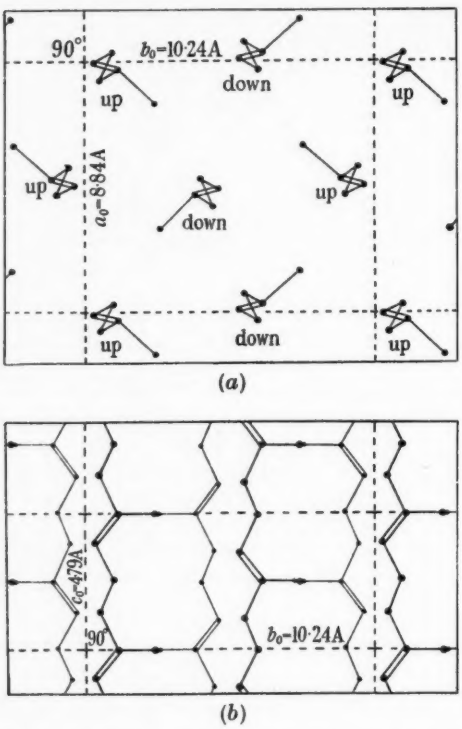


FIG. 8.—Crystal structure of polychloroprene, seen (*a*) along *c* axis, (*b*) along *a* axis.

APPENDIX

GRAPHICAL METHOD OF DETERMINING INTENSITIES FOR HKL PLANES

Bragg and Lipson[30] devised charts for determining the structure factors for planes of the type *hk*0, 0*kl* and *h*0*l*. These can also be used for shortening the work of calculating the structure factors for *hkl* planes.

For example, in β-gutta-percha and polychloroprene the space group is $P\ 2_12_12_1$, for which the structure factor is $\sqrt{(A^2+B^2)}$, where

$$A=\Sigma 4f\cos 2\pi\left(hx-\frac{h-k}{4}\right)\cos 2\pi\left(ky-\frac{k-l}{4}\right)\cos 2\pi\left(lz-\frac{l-h}{4}\right)$$

(summed for all atoms),

$$B=-\Sigma 4f\sin 2\pi\left(hx-\frac{h-k}{4}\right)\sin 2\pi\left(ky-\frac{k-l}{4}\right)\sin 2\pi\left(lz-\frac{l-h}{4}\right)$$

(summed for all atoms).

The *xy* positions of the atoms are plotted on a transparent square chart in the manner given by Bragg and Lipson[30]; the *z* positions are plotted in a separate strip. To find *A*, the product of the first two cosine terms is read off on a chart giving cos $2\pi hx$ cos $2\pi ky$ (plane group *Pba*) by suitably displacing the origin; for instance, for plane 231, $2\pi\left(\frac{h-k}{4}\right)$ is $-90°$ and $2\pi\left(\frac{k-l}{4}\right)$ is $+180°$; using the 230 chart, the origin of the atomic position chart is shifted 90° back-

wards along the x axis and 180° forwards along the y axis. The last cosine term is read off on the strip, using a one-dimensional chart giving cos $2\pi lz$; for plane 231, $2\pi\left(\frac{l-h}{4}\right)$ is $-90°$, and the origin of the strip must therefore be displaced backwards 90°. The only calculation is then the multiplication of the two graphically estimated figures and f, the diffracting power of the atom. Since terms are obtained in a similar way from the same charts.

This procedure is of course longer than for planes of type $hk0$, etc., but it is very much shorter than straightforward calculation of hkl structure factors.

The space group of rubber is $P\ 2_1/a$, for which the structure factor is:

$$A=4\cos 2\pi\left(hx+lz+\frac{h+k}{4}\right)\cos 2\pi\left(ky-\frac{h+k}{4}\right)\quad(B=0).$$

The x and z positions of the atoms are plotted on square chart, and the first cosine term read off on the Bragg and Lipson chart for plane group $P\ 2$, the origin being displaced by $2\pi\left(\frac{h+k}{4}\right)$; the y positions are plotted on a strip as in the previous example, and the second term read off, again after the appropriate displacement of the origin; the two terms are then multiplied.

TABLES OF RESULTS

In accordance with a recent recommendation of the Royal Society (30 March 1939), tables of figures in connection with the crystal structure determinations are not included in the paper itself, but are given separately.

The figures given in the following tables are the relative intensities calculated for x-ray diffractions from the various crystal planes, assuming the atomic positions given in the paper. The figures are proportional to $p[\theta]\,F^2$, where F is the structure factor (see below), $[\theta]$ the angle factor (for instance, $\frac{1+\cos^2\theta}{\sin^2\theta}$ for the equatorial spots of a fibre photograph), and p the number of coöperating crystal planes. For nonequatorial spots Cox and Shaw's correction factors were used[31].

The structure factor for space group $P\ 2_12_12_1$ (the space group of β-guttapercha and polychloroprene) is $\sqrt{(A^2+B^2)}$, where

$$A=\Sigma 4f\cos 2\pi\left(hx-\frac{h-k}{4}\right)\cos 2\pi\left(ky-\frac{k-l}{4}\right)\cos 2\pi\left(lz-\frac{l-h}{4}\right),$$

$$B=-\Sigma 4f\sin 2\pi\left(hx-\frac{h-k}{4}\right)\sin 2\pi\left(ky-\frac{k-l}{4}\right)\sin 2\pi\left(lz-\frac{l-h}{4}\right).$$

For space group $P\ 2_1/a$ (that of rubber), the structure factor is:

$$A=\Sigma 4f\cos 2\pi\left(hx+lz+\frac{h+k}{4}\right)\cos 2\pi\left(ky-\frac{h+k}{4}\right),\quad B=0.$$

For f, the diffracting power of an atom, the values given for uncharged carbon and chlorine atoms by Bragg[32] were used. The diffracting powers of CH, CH_2 and CH_3 groups were assumed to have diffracting powers $\frac{7}{6}$, $\frac{8}{6}$, and $\frac{9}{6}$ that of carbon itself, these figures being proportional to the number of electrons in

each group. This is strictly true only for small angles of diffraction, but at any angle it is a better approximation to the truth than the assumption of equal diffracting powers for these groups.

No corrections have been made for the thermal vibrations of the atoms.

β-Gutta-Percha

The three columns in each section give the indices, calculated intensity, observed intensity.

A. *Normal Fibre Photograph*

		*hk*0	170	0.1	—	051	1.0	—
110	0.2	—	440	0.2	—	241	3.1	—
020	4.6	vw	360	5.2	vvw	151	0.2	—
120	325.0	vs+	270	0.1	—	331	3.6	—
200	207.0	vs	510	0.1		251	3.5	—
210	3.9	—				061	2.2	—
130	0.3	—				341	1.0	—
220	5.5	vw			*hk*1	401	2.3	—
040	24.8	m	011	74.0	ms	411	13.6	w
230	1.7	ms	101	0.6	—	161	1.8	
140	38.1		111	8.9	vw	421	1.6	—
310	0.1	—	021	0.2	—			
320	9.8	m	121	10.7	—			
240	12.2		031	15.9	w		*hk*2	
150	0.2	—	201	5.6		112	26.0	w
330	0.6	—	211	32.8	ms	022	52.0	
250	0.5	—	131	3.1	—	122	2.0	—
060	7.2	w	221	1.2	—	032	0.2	w
340	6.0	w	041	1.8	—	202	11.2	
400	7.0		231	6.7	vw	212	6.0	
410	2.6	m	141	1.4		132	9.7	
160	28.6		301	1.0	w	222	29.1	
420	0.6	—	311	7.1		042	0.0	—
260	6.9		321	2.0	—	232	8.7	—
350	0.7	vvw				142	2.5	—
430	1.6							

B. *Fibre axis oscillating 90°–45° to x-ray beam*

	hkl		023	0.0	—
002	5.4	mw	004	0.5	vw
012	1.8	—	014	3.1	
102	0.8		104	0.0	
013	1.5	vvw			
103	0.2				
113	0.5				

For all reflections *h*00 with *h* odd, 0*k*0 with *k* odd, and 00*l* with *l* odd, the observed and calculated intensities are nil.

vs + = extremely strong, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, vw = very weak, vvw = extremely weak.

Rubber

A. *Normal Fibre Photograph*

	*hk*0		830	0.0	—	$\bar{3}31$	0.4	
110	1.5	—	910	0.0	—	$\bar{5}11$	0.0	vvw
200	64.3	s	650	0.0	—	331	1.0	
210	0.3	—	460	2.0	—	511	0.3	
020	0.2	—	920	15.0	vw	041	0.7	—
120	254.0	vs+	840	1.0	—	$\bar{5}21$	1.0	—
310	0.6	—	560	0.3	—	$\bar{1}41$	2.1	
220	5.0	—	170	0.0	—	141	0.0	
400	15.0	m	750	0.0	—	$\bar{4}31$	4.0	vw
320	4.0		930	0.0	—	521	0.4	
410	0.2	—	10.0.0	7.3	vvw	431	0.0	
130	0.1	—	270	0.0	—	$\bar{6}01$	0.4	w
230	0.2	—	10.1.0	0.0	—	$\bar{2}41$	5.8	
420	0.2	—	370	0.0	—	241	1.0	
330	0.4	—	660	0.6	—	601	0.6	
510	0.0					$\bar{6}11$	0.5	—
040	25.7	m				611	0.4	
140	0.0	—				$\bar{3}41$	0.0	—
520	4.6					341	1.5	
430	0.0	—		*hk*1		$\bar{5}31$	0.3	—
240	1.2	—	011	0.7	—	621	0.0	—
600	0.0		$\bar{1}11$	2.0	vw	531	0.0	
610	0.0	—	111	2.3		621	0.9	—
340	0.0	—	$\bar{2}01$	22.0	s	$\bar{4}41$	0.4	—
530	0.0	—	201	26.4		441	0.6	—
620	0.0	—	$\bar{2}11$	3.3	—	051	0.0	—
440	0.0	—	211	1.6		$\bar{1}51$	2.0	vw
150	1.4	—	021	2.9	—	151	0.1	
710	0.0	—	$\bar{1}21$	31.1	s	$\bar{7}11$	1.3	
250	0.0	—	121	22.2		711	0.9	
630	0.0		$\bar{3}11$	6.5	mw	$\bar{6}31$	0.0	—
540	1.8	—	311	4.1		$\bar{2}51$	0.0	
720	0.0		$\bar{2}21$	1.8	—	251	0.0	
350	0.8	—	221	1.5		631	0.4	—
800	4.6	vvw	$\bar{4}01$	0.0	—	$\bar{5}41$	0.6	vw
450	0.0		401	0.0	vw	$\bar{7}21$	0.4	
730	0.0		$\bar{3}21$	0.5		541	0.0	
810	0.0	—	321	0.0		$\bar{3}51$	1.5	
640	0.4	—	$\bar{4}11$	0.2		721	0.6	
060	0.1	—	031	2.8		351	2.8	
160	1.8	—	$\bar{1}31$	0.2	—	$\bar{8}01$	1.0	vw
820	0.0	—	411	0.5		$\bar{7}31$	0.2	
550	0.0	—	131	0.3		$\bar{4}51$	0.0	
260	0.1	—	$\bar{2}31$	2.4	mw	801	0.9	
360	0.3	—	231	2.8		451	0.0	
740	0.0	—	$\bar{4}21$	0.0	—	731	0.2	
900	0.0	—	421	1.0				

*hk*2						*hk*4		
012	6.9	mw	$\bar{2}42$	0.0	—	014	5.3	
$\bar{1}12$	4.3		242	0.1		$\bar{1}14$	0.0	w
112	1.4	—	$\bar{6}12$	1.6	vvw	$\bar{2}04$	0.0	
$\bar{2}02$	23.6	ms	602	0.0		114	0.0	
202	29.4		612	2.8		204	0.5	—
$\bar{2}12$	0.4	—				$\bar{2}14$	0.0	—
212	2.9	—				214	0.0	—
022	5.8	m				024	0.0	—
$\bar{1}22$	0.0					$\bar{1}24$	5.0	
122	0.6	—				124	6.3	mw
$\bar{3}12$	2.8					$\bar{3}14$	0.0	
$\bar{2}22$	0.0	m				$\bar{2}24$	0.3	
312	4.6					314	0.0	
222	0.0		*hk*3			224	1.4	—
$\bar{4}02$	1.1	vvw	013	0.0	—	$\bar{4}04$	0.8	—
$\bar{3}22$	1.3		$\bar{1}13$	2.0		$\bar{3}24$	0.0	
402	0.6	—	$\bar{2}03$	1.0	mw	$\bar{4}14$	1.3	
$\bar{4}12$	6.7		113	20.0		034	0.9	
032	0.1		203	1.5	—	404	0.4	vw
322	2.0	mw	$\bar{2}13$	0.0		$\bar{1}34$	0.0	
$\bar{1}32$	0.2		213	0.0	—	324	0.6	
132	0.8		023	6.3		134	0.8	
412	6.5		$\bar{1}23$	3.7	mw	414	0.4	
$\bar{2}32$	0.2		123	8.8				
232	0.0	vvw	$\bar{3}13$	1.0				
$\bar{4}22$	0.0		$\bar{2}23$	0.4	—			
422	0.0	—	313	0.2	—			
$\bar{5}12$	8.2		223	7.2				
$\bar{3}32$	0.8	m	$\bar{4}03$	2.6				
332	0.8		$\bar{3}23$	4.7				
512	4.1		$\bar{4}13$	0.0				
042	1.7		403	2.0				
$\bar{5}22$	1.6		033	2.7	mw			
$\bar{1}42$	0.7		323	1.5				
$\bar{4}32$	1.0	m	$\bar{1}33$	1.6				
142	0.0		133	0.7				
522	2.3		413	0.0				
$\bar{4}32$	3.0		$\bar{2}33$	0.0	—			
$\bar{6}02$	0.0		$\bar{4}23$	1.1	—			

B. *Fibre Axis Oscillating 90°–45° to X-ray Beam*

00l			*hk5*					
001	0.2	vvw	005	0.0	—	$\bar{0}25$	0.0	vw
002	8.0	mw	015	0.1	—	$\bar{1}25$	2.2	
003	0.0	—	$\bar{1}15$	0.0	vw	$\bar{3}15$	0.3	
004	9.2	mw	$\bar{2}05$	1.1		125	0.8	
			115	0.0		$\bar{2}25$	0.1	
			$\bar{2}15$	0.0	—	315	0.6	
			205	0.7		225	0.0	
			215	0.0	—			

For all reflections $0k0$ with k odd, $h00$ and $h0l$ with h odd, the observed and calculated intensities are nil.

Polychloroprene

A. *Normal Fibre Photograph*

hk0										
110	1.8	w	430	4.8	mw	031	7.0	mw		
020	0.5	—	250	4.0		221	7.3			
200	5.5	vs	510	0.1	—	131	0.2	—		
120	25.8		060	2.9	vvw	301	0.1	—		
210	18.6	s	350	0.0	vvw	311	0.1	—		
220	15.7	s	160	0.2		231	0.3	—		
130	1.2	—	440	1.3		041	0.0	—		
310	1.3	—	520	0.2		321	0.9			
230	3.2	w	260	0.0	—	141	0.0	—		
040	1.8	w	530	0.0	—					
320	2.2									
140	3.5	vw	*hk1*			*hk2*				
330	0.2	—	011	32.0	ms	112	1.0	mw		
240	3.1	vw	101	0.0	—	022	23.0			
400	0.0		111	0.2	—	202	1.3	—		
410	2.9	vvw	021	0.2	—	122	1.6			
420	2.5	vvw	201	4.4	w	212	8.0			
150	0.1	—	121	0.7		032	2.2	—		
340	1.5	—	211	4.0		222	0.6			

B. *Fibre Axis Oscillating 90°–45° to Beam*

hk2		
002	3.3	mw
012	0.1	—
102	0.0	—

For all reflections $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd, the observed and calculated intensities are nil.

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MOLECULAR STRUCTURE AND RUBBER-LIKE ELASTICITY

II. THE STEREOCHEMISTRY OF CHAIN POLYMERS *

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In Part I of this work[1], the determination of the crystal structures of three long-chain polymers by interpretation of x-ray diffraction photographs was described. In all three crystals—β-gutta-percha, rubber and polychloroprene—the molecules have nonplanar zigzag chain forms and are asymmetric. It is now necessary to consider the bearing of the new knowledge of molecular geometry on the possibility of understanding rubber like properties in terms of molecular physics. It is widely believed that the flexibility, softness and other characteristic properties of rubberlike substances are in some way due to the flexibility of the molecules themselves. Long-chain molecules owe their potential flexibility to the swivelling of the chain units around the single bonds as axes, and it is therefore necessary to consider which bond positions are the most stable and what hindrances there are to rotation away from these positions. The present paper deals chiefly with the question of the most stable bond positions. The enquiry has interest, not only in relation to the problem of the origin of rubberlike properties, but also because it opens the way to a systematic consideration of chain types. There is already evidence that in many crystalline long-chain polymers, such as rubber hydrochloride[2], polyisobutylene[3], and some of the polyesters[4], the chains have not the fully extended plane zigzag form of polyethylene[5], but somewhat shortened (necessarily nonplanar) forms. It should be possible to discover what these forms are by interpretation of x-ray diffraction photographs, but the difficulties are in some cases formidable; some assistance in the form of guiding principles for the construction of possible chain types is desirable. It is the purpose of this paper to show that sufficient evidence already exists to suggest a general principle regulating bond positions in aliphatic molecules containing sequences of singly linked atoms. It will be called the principle of staggered bonds.

In the three molecules whose structures were determined in Part I, every fourth chain bond is a double bond; the question of bond positions is less simple for such molecules than it is for those in which all the bonds are single. The latter will therefore be considered first.

BOND POSITIONS IN SATURATED MOLECULES

A survey of all the well-established structures of simple, saturated organic molecules, whether in the gaseous state or in crystals, has been made, and has shown that the favored positions of the bonds of two singly linked carbon atoms are as shown in Figure 1. The tetrahedral angles between the bonds of any one carbon atom are preserved (within a few degrees), and the two trios of bonds *abc* and *a′b′c′* of two singly linked carbon atoms are staggered with

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respect to each other. Thus, for ethane, both the electron diffraction pattern[6] and the infrared absorption spectrum[7] suggests that the two trios of hydrogen atoms spend most of their time in the staggered position; they undoubtedly rotate around the C−C bond as axis, but the rotation is not a revolution at constant speed, or a random rotation, but a rapid switching from one to another of the three equivalent positions.

In 1,2-dichlorethane, CH_2ClCH_2Cl, both x-ray diffraction patterns[8] and electron diffraction patterns[9] indicate that the halogen atoms spend most of their time at the maximum possible distance from each other, *i.e.*, with the C−Cl bonds at positions *a*, *a'* of Figure 1. The same is true for the corresponding dibromoethane, CH_2BrCH_2Br, and for the chlorobromo compound, CH_2ClCH_2Br[10]. There is some indication that there may be alternative positions with the C−C−*X* planes at 80° to each other, in addition to the most frequent position with these planes at 180°. An angle of 80° means 20° deviation from alternative staggered positions *ab'* or *ac'* of Figure 1; the deviation may be due to mutual repulsion of the halogen atoms (the electric dipole moment of C−Cl is high).

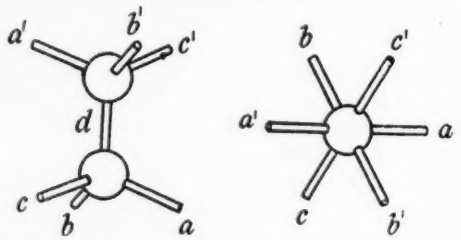

FIG. 1.—Bond positions in saturated molecules.

That there are alternative positions in CH_2ClCH_2Cl is shown also by the appearance in the Raman spectrum of a doublet for the C−Cl vibration; the two components of the doublet have different intensities at room temperature, showing that one position (the 180° position according to x-ray and electron diffraction patterns) is favored, but the intensities become more nearly equal with rise of temperature, showing that the second position is visited relatively more frequently at higher temperatures[11].

In 1,1,2-trichlorethane, $CHCl_2CH_2Cl$, the angle between the planes $Cl-C^1-C^2$ and C^1-C^2-Cl is 70°—within 10° of the precise staggered position[12]; and in $Br(CH_3)CHCH(CH_3)Br$ the staggered position is again the most stable, the bromine atoms being in positions *aa'* of Figure 1[13]. In cyclohexane there are only two structures which allow tetrahedral angles between the carbon bonds; the "chair" and "boat" forms of Sachse. It is interesting to find that in gaseous cyclohexane the molecules have the chair form, in which all the bonds are staggered (Figure 2*c*); the boat form, in which the bonds are opposed, does not occur[6]. In trimethylmethane[14] and in tetramethylmethane[6], there is some indication that the hydrogen atoms of the methyl groups may be most frequently at positions 30° from the staggered position, *i.e.*, halfway between the staggered and opposed configurations. The evidence for all these molecules is provided by the electron diffraction patterns of the gases.

In crystals, likewise, the staggered configuration is favored. The plane zigzag of carbon atoms in long-chain normal paraffin hydrocarbons such as polyethylene (Bunn[5]) is simply a repetition of the plane zigzag *ada'* (or *bdb'* or

cdc') of Figure 1, and assuming that the hydrogen atoms are in the tetrahedral positions, all the bond orientations in the molecule (see Figure 2*a*) conform to the model of Figure 1. In pentaerythritol, $C(CH_2OH)_4$[15], and its tetraacetate[16], we find the same scheme of bond orientation (Figure 2*b*), and in diamond[17] the scheme attains its most extended expression, a perfect diamond crystal (Figure 2*d*) being simply a gigantic molecule composed of carbon atoms all linked together in precisely the manner shown in Figure 1. The carbon atoms of succinic acid, $HOOCCH_2CH_2COOH$, form a plane zigzag as in the normal paraffin hydrocarbons[18]. The same is true for the tartrate ion in Rochelle salt[19].

In 1,2-diiodoethane, CH_2ICH_2I, the distance between the iodine atoms[20] leaves little doubt that they are at the maximum possible distance from each other, *i.e.*, the C—I bonds are at positions *aa'* of Figure 1. Similarly, the positions of

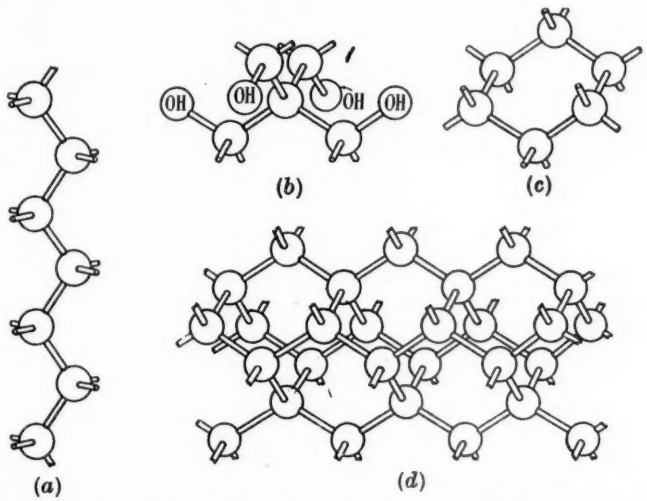

FIG. 2.—Structures of some singly-linked molecules. (*a*) Normal paraffin hydrocarbons. (*b*) Pentaerythritol. (*c*) Cyclohexane. (*d*) Diamond.

the halogen atoms in the crystalline hexachloro and hexabromo derivatives of cyclohexane[21] indicate strongly that the carbon ring (like that of gaseous cyclohexane) has the chair form, in which the bonds of linked carbon atoms are staggered (Figure 2*c*)[22].

REASON FOR THE STAGGERED CONFIGURATION

The number of instances in which the staggered configuration is the most stable is sufficient to suggest that it may be a quite general rule which regulates the bond positions on successions of singly linked carbon atoms, just as Van't Hoff's tetrahedral model specifies the bond positions on any one carbon atom. In this connection it is relevant to enquire into the reason for the staggered configuration. The tetrahedral disposition of the bonds of any one carbon atom is primarily due, not to mutual repulsion of the atoms or groups held by the bonds, but to a strong orienting tendency of the bonds themselves (the shared electron links being most stable when tetrahedrally disposed), and it may be that the staggered configuration of the bonds of linked carbon atoms is due to

a similar orienting tendency of the bonds themselves. Although there is no clear evidence on this point, one influence—the effect of electric dipole moments—may be discounted; in the molecule of 1,1,2-trichlorethane, $CHCl_2CH_2Cl$, all the electric dipole moments H^+-C^- and C^+-Cl^- favor the opposed configuration; *i.e.*, if the configuration were determined mainly by the dipole moments, the angle between the planes $Cl-C^1-C^2$ and C^1-C^2-Cl would be 120°, giving the maximum distances between the chlorine atoms. Actually (Figure 3) the angle is 70°, within 10° of the staggered bond position; there are two 70° positions between which oscillation occurs. Evidently the electric dipole effect is small; the staggered bond configuration is, therefore, due either to an orienting tendency of the bonds themselves or to atomic interactions not attributable to electric dipole effects, or to both these factors. Kistiakowsky, Lacher and Ransom[23] have suggested that, quite apart from the question as to which configuration is the most stable, the potential barrier to rotation is due to interaction between the electron pairs constituting the bonds. It should perhaps be mentioned that quantum-mechanical calculations of the forces in the ethane molecule have recently been made by several investigators. Some of these appear to point to the opposed configuration as the more stable; but the problem is a complex

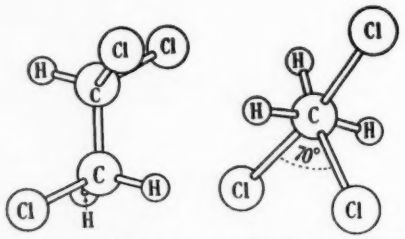

FIG. 3.—Molecular structure of 1, 1, 2-trichlorethane $CHCl_2 . CH_2Cl$.

one, and different authors do not agree about the contributions of various factors[24]. The theoretical treatment must therefore be regarded as tentative. Meanwhile, the experimentatal evidence must be accepted, which is strongly in favor of the general stability of the staggered configuration. The barrier to rotation is 3000 calories in ethane[25] and at least 5000 calories in 1,1-dichlorethane and similar molecules[26].

Deviations from the staggered positions must be expected when the bonds hold atoms or groups of very different sizes, or still more when the atoms take part in certain ring structures. Thus, in cyclopentane, the carbon atoms form a plane ring, in which the bonds are opposed, not staggered[6]. The reason is, no doubt, that the preservation of the tetrahedral angles between the bonds on any one carbon atom is a more urgent necessity than the maintenance of the staggered bond scheme for successive carbon atoms.

PREDICTION OF STRUCTURES OF SATURATED MOLECULES

If the principle of staggered bonds is of general validity (with the reservations mentioned in the last paragraph), it can be used for predicting the possible configurations of saturated molecules. It will not, in general, indicate only one possible structure for any particular molecule, because alternative bond positions will (except in the simplest molecules) give rise to different configurations; but it will usually indicate a limited number of possible structures, each

of which can be tried out in turn. A useful way of regarding the possible single-bonded structures comes from the realization that all single-bonded carbon structures which conform to Figure 1 are portions of the diamond structure (Figure 2*d*). It is not to be expected that the precise geometry of any particular structure can be predicted, because the interaction of different groups will give rise to distortions of the ideal model; but an approximate prediction is better than no prediction at all.

In attempting to predict the structure of any particular molecule, it will be necessary to consider first the possible alternative bond-sequences, to select if possible the most probable of these, and then to consider what distortions of the ideal model are likely to occur.

For large molecules there may be many possible bond sequences, but it will often happen that consideration of atomic radii and the clearances between different parts of the molecule will show that one bond sequence is more probable than all others. As an example, consider how the simple plane zigzag chain of the normal paraffin hydrocarbons arises. Any two chain bonds such as *a'* and *d* in Figure 1 are at the tetrahedral angle to each other. For the next chain bond there are three possible positions, *a*, *b* and *c*. If it took up position *b*, the carbon atoms on *a'* and *b* would be only 2.9 A.U. apart; since the radius of a CH_2 group is 1.8–2.05 A.U., it is evident that there would be considerable repulsion between the groups in these positions. The same is true for bond position *c*, which is exactly equivalent to *b* in this respect. In position *a*, however, the carbon atoms on *a'* and *a* are at the maximum possible distance from each other (3.9 A.U.); this position is therefore more probable than the other two. The same applies to all the chain bonds, hence the most probable chain configuration is the plane zigzag (Figure 2*a*). This is the structure which chains of CH_2 groups are likely to have at low temperatures, and thus it is not surprising that this is the structure we find in crystalline normal paraffin hydrocarbons.

NOMENCLATURE OF CHAIN TYPES

When side substituents are present on a carbon chain, the plane zigzag may not be the most probable form of chain. It will be useful to have a simple way of referring to different chain types. For any three chain bonds, we have seen that there are three different configurations, *a'da*, *a'db* and *a'dc;* these will be called *A*, *B* and *C*, respectively. Repetition of *A* gives the plane zigzag (Figure 2*a*) which has an identity period of 2.53 A.U.; this chain is best symbolized *AA* or A_2, since this indicates the two-atom identity period as well as the bond sequence. Other chain types are illustrated in Figure 4. Repetition of *B* gives rise to a right-handed spiral chain *BBBB* or B_4 with a four-atom period of 3.6 A.U.; in the end-view of this chain, the atoms fall at the corners of a square. Repetition of *C* gives the corresponding left-handed spiral C_4.

Alternation of *A* and *B* gives rise to a left-handed spiral chain $(AB)_3$ with a six-atom period of 6.2 A.U.; in the end-view, the chain atoms fall at the corners of an equilateral triangle. Alternation of *A* and *C* gives the corresponding right-handed spiral $(AC)_3$. Alternation of *B* and *C* gives the cyclohexane ring $(BC)_3$, already illustrated in Figure 2*c*. Other simple chain types which are not spirals, but merely nonplanar zigzags, are also shown in Figure 4.

DETERMINATION OF CHAIN TYPE IN CRYSTALLINE POLYMERS

These chain types arising from regular repetitions of particular bond sequences are those likely to be found in crystalline chain polymers. Each chain

type has its own characteristic identity period, and the identity periods of the simpler types are quite different from each other (see Figure 4). Evidently it should be possible to find the type of chain in a polymer molecule by mere determination of the identity period of the molecule; this is quite easily found from the x-ray (or electron) diffraction patterns of crystalline chain polymers, since in a stretched or rolled out specimen the identity period of the crystals in the direction of stretching or rolling (calculated directly from the distance between the layer lines on the diffraction pattern) is the identity period of the molecules themselves. The figures given are ideal identity periods, based on the precise staggered bond model of Figure 1. Some departure from these figures may be

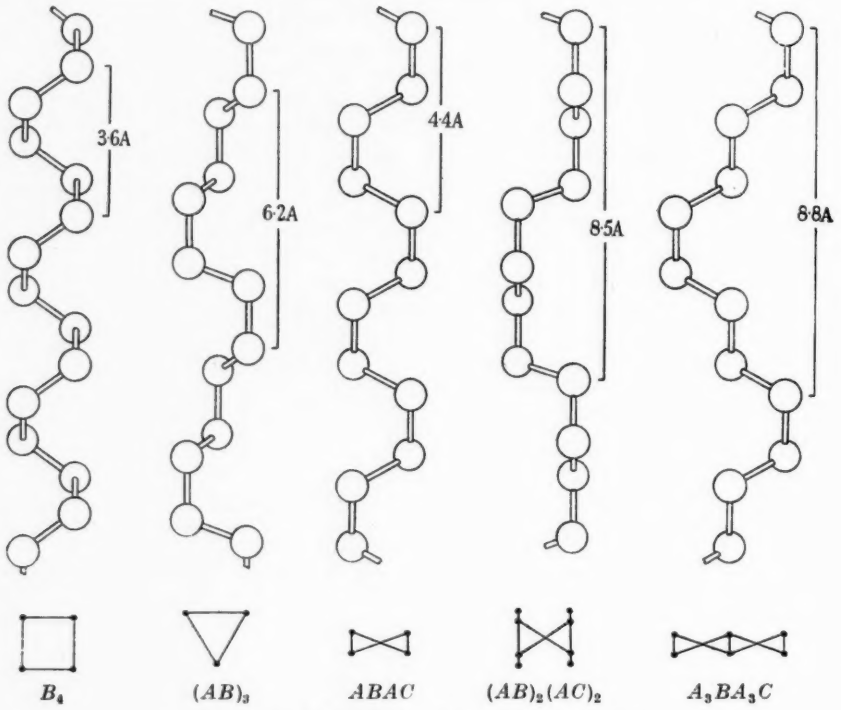

FIG. 4.—Some of the simpler single-bonded chain-types.

expected, although not enough to lead to uncertainty for the simpler chain types.

When a chain polymer is found to have a long identity period, more than one chain type may appear eligible; for with increase in the number of atoms per period the number of different bond sequences (some with similar identity periods) increases rapidly. In such cases, knowledge of the chemical structure of the chain molecules may help towards the selection of the correct chain type; each chemical unit in the chain would be expected to have a similar configuration, and thus the chemical structure of the chain would be reflected in the bond sequence. (For this purpose, enantiomorphic configurations such as *AB* and *AC* are equivalent.) As an example, rubber hydrochloride, which is believed to be chemically $(-CH_2-CH_2-CH_2-C(CH_3)Cl-)_n$, is a crystalline substance with a molecular identity period of 9.1 A.U.[2] The chain structure A_3BA_3C (Figure 4)

is suggested for this molecule, since 9.1 A.U. is sufficiently near the ideal period of 8.8 A.U., and the bond sequence is compatible with the chemical structure of the molecule[27].

STRUCTURES CONTAINING POLYVALENT ATOMS OTHER THAN CARBON

The amount of evidence on molecules containing nitrogen, oxygen and sulfur atoms bonded with carbon is less than that relating to carbon-carbon links, but what evidence there is suggests that in these molecules also the principle of staggered bonds is obeyed. This would perhaps be expected, because these atoms are stereochemically similar to carbon, having their bonds fixed at the tetrahedral angle to each other, and therefore the interactions of the bonds of successions of any of these atoms might be expected to be similar to those of carbon sequences.

The only evidence on nitrogen compounds is that the identity periods of polyhexamethylene adipamide, $(-NH(CH_2)_6.NH.CO.(CH_2)_4.CO-)_n$[4], and natural silk, $(-CHR.CO.NH-)_n$[28] are such that the chains must be plane or nearly plane zigzags similar to the carbon chain in normal paraffin hydrocarbons; and the bond structure of hexamethylenetetramine, $(CH_2)_6N_4$, is the same as that of a portion of the diamond structure[29].

The oxygen and sulfur compounds which have been examined are pentaerythritol tetraacetate, $C(CH_2O.CO.CH_3)_4$, in which the singly linked oxygen atoms participate in plane zigzag chains[16]; trimethylene oxide, $(CH_2O)_3$, and the corresponding sulfur compound, $(CH_2S)_3$, which have ring structures with chair forms like cyclohexane[30]; paraldehyde $(CH_3.CHO)_3$, which probably has the same ring structure[31]. In all these, the bonds are staggered. In metaldehyde, $(CH_3CHO)_4$, the molecules are nonplanar eight-atom rings, in which there is some deviation from the staggered bond positions. The identity periods of some of the polyesters, $(-CO-(CH_2)_x-CO-O-(CH_2)_y-O-)_n$, indicate that the chains are nearly fully extended zigzags like $(CH_2)_n$[4]; there cannot be much deviation from the staggered positions here.

Assuming that the staggered positions are favored in such molecules, configurations for molecules containing these atoms can be predicted. The chain forms illustrated in Figure 4 are valid for chains containing these atoms, although the identity periods will necessarily be different. It has been remarked[32] that the identity periods of certain long-chain polyesters indicate that the chains cannot be plane zigzags; for instance, polyethylene-succinate,

$$(-CO-CH_2-CH_2-CO-O-CH_2-CH_2-O)_n,$$

has an identity period of 8.3 A.U., whereas a plane zigzag chain would have a period of 9.8 A.U. The nonplanar zigzag chain form which has been suggested for this molecule by Fuller & Erickson[32] is actually *ABAC* illustrated in Figure 4. (The period for the molecule is necessarily twice *ABAC* on account of the chemical constitution of the molecule.) These authors consider that this chain configuration results simply from attractions of atoms or dipoles placed at intervals along the chain. The present point of view is that the possible chain forms are determined by the principle of staggered bonds, although the choice by any particular molecule of one chain form rather than another no doubt depends on attractions or repulsions of certain atoms or groups not only in the same molecule but also in neighboring molecules in the crystal. *ABAC* is not the only chain form possible for this molecule; $(AB)_2(AC)_2$ (Figure 4) seems also eligible.

The complex chain forms of polyoxymethylene, $(-CH_2-O-)_n$, and polyoxyethylene, $(-CH_2-CH_2-O-)_n$, probably result also from the operation of the principle of staggered bonds, combined with the effects of the interactions of particular atoms or dipoles. The identity periods—17.35 and 19.5 A.U., respectively, each containing nine chemical units[33]—seem remarkably long for molecules of such essentially simple chemical structure; but it must be remembered that comparatively simple bond sequences may lead to long identity periods. Repetition of *ABABAC* leads to an 18-atom period $(ABABAC)_3$ of about 17.5 A.U., this seems a possible chain form for polyoxymethylene.

BOND POSITIONS IN UNSATURATED MOLECULES

This enquiry started as an attempt to understand the nonplanar chain forms of three unsaturated polymer molecules; it was undertaken as a necessary step in the approach to the question of molecular flexibility. Now return to these unsaturated chains, and consider them against the background of the principle

FIG. 5.—Bond positions in group >C=C<.

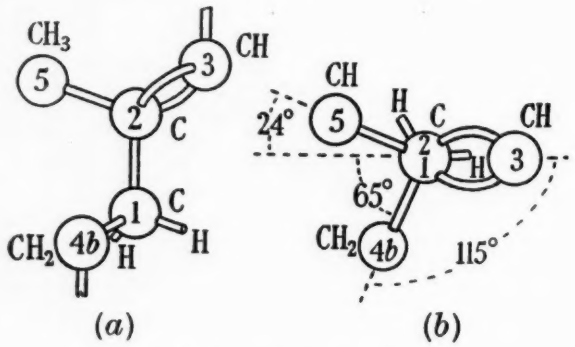

FIG. 6.—Bond positions in β gutta-percha.

of staggered bonds. The interest centres on the positions of the single bonds, (CH_2-CH_2), which join isoprene or chloroprene units,

$$(-CH_2-CR=CH-CH_2-).$$

But first of all the configuration of the isoprene and chloroprene units themselves needs some comment.

Each such unit is roughly planar (see Figures 2, 4 and 7 of Part I). This is in accordance with expectation, since in ethylene[34] and its chloro substitution products[35], all the atoms lie in a plane—a configuration consistent with the simple geometrical concept of the double bond shown in Figure 5. There are, however, some large distortions, the greatest being those of the bonds holding methyl groups or chlorine atoms. Thus, in β-gutta-percha the bond holding the methyl group lies over 20° out of the plane $CH_2-C=CH$ (see Figure 6). In rubber, the distortions are different in the two isoprene units which make up the molecular identity period; the greatest is as much as 35°. In polychloroprene, whose molecular structure is analogous to that of β-gutta-percha, the corresponding distortion of the C−Cl bond is even higher *viz.*, 40°. These distortions appear to be due chiefly to repulsion between the methyl or chlorine side-

substituent and one of the chain CH_2 groups (5 and 4*b* in Figure 6). But in rubber, since the configurations of the two isoprene units in its period are different, the distortions must be due partly to the effect of packing together the awkwardly shaped molecules; each molecule is distorted by the other molecules surrounding it; the van der Waals' forces of attraction responsible for holding the molecules together in a precise crystalline formation are strong enough to give rise to very appreciable distortions of bond positions.

These distortions are surprisingly large. It is well established (by the great stability of *cis* and *trans* isomers) that rotation around a double bond requires a high energy—a state of affairs well illustrated by the traditional simple geometrical picture of the double bond shown in Figure 5—and therefore it might have been expected that the single bond positions would be severely restricted. This is not so; evidently distortions up to 40° are fairly easily brought about.

Now return to the main question—the reasons for the positions of the single CH_2-CH_2 bonds which join isoprene or chloroprene units together. These bonds make large angles with the $CH_2=C-CH$ planes, and give the chains their pronouncedly nonplanar character. In β-gutta-percha, plane CH_2-CH_2-C makes an angle of 115° with plane $CH_2-C=CH$ and 89° with plane CH_2-C-CH_3 (see Figure 6*b*). In polychloroprene, the angles are not very different. In rubber, the two isoprene units in the period have different configurations; in one of them, the angles specified are 109 and 86°; in the other they are 169½ and 45½°. These bond positions are, no doubt, partly due to the presence of the substituent methyl group or chlorine atom; owing to its presence, the CH_2 chain group cannot be in the plane of the isoprene unit, but is pushed to one side. Thus the same repulsion which is responsible for pushing the methyl group away from the $CH_2-C=CH$ plane (the repulsion between CH_3 group 5 and CH_2 group 4*b* in Figure 6) is also responsible, at any rate partly, for the pronouncedly nonplanar character of the chain. But in view of the preference for the staggered bond configuration in singly linked molecules—a preference which, it is suggested, is due largely to an orienting tendency of the bonds themselves rather than to interactions between the atoms held by the bonds—the question arises whether there is a similar influence in the unsaturated molecules under discussion. From this point of view, it is interesting to note that, in β-gutta-percha, if the double bond is represented in the simple geometrical way shown in Figure 6, then the three bonds of atom 2 are staggered with respect to those of atom 1; this is shown most clearly in Figure 6*b*. There is some distortion, but still an approximation to the staggered configuration, if it is justifiable to regard the double bond as two distorted single bonds. In polychloroprene, the bond positions are very similar to those in β-gutta-percha. In rubber, the bond orientation for one-half the isoprene units is again similar, but in the other half the angles (given above) are considerably different from those in β-gutta-percha. It is evident that, if we are correct in supposing that there is some tendency towards the staggered bond configuration (which, together with the repulsions between atomic groups, is responsible for the nonplanar character of the chain) nevertheless this configuration is easily distorted; in rubber crystals, the distortion is brought about by the van der Waals' forces between adjacent molecules.

Ease of distortion is bound up with the magnitude of the potential barrier to rotation; there is some evidence of this magnitude in simple gas molecules, and it is interesting to find that in those containing the bond sequence, $-C-C=C$, the barrier to rotation is much lower than in saturated molecules.

Thus, in propylene, $CH_3-C\begin{matrix}H\\ \| \\ CH_2\end{matrix}$ [23], and in acetone, $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C=O$ [36], the barrier of rotation of the methyl group is not more than 1000 calories—only one-third the figure for ethane and other saturated molecules. It has been suggested[23] that this indicates that the double bond has no orienting influence; the rotation of each methyl group in propylene and acetone is perhaps restricted by only one single bond—the H−C bond in propylene (compared with three in saturated molecules), and this may be the reason why the restricting potential has only one-third the value found in saturated molecules. However this may be, the smallness of the potential barrier to rotation in such groupings is presumably the reason why the staggered bond configuration is so easily distorted in rubber molecules.

In view of the experimental evidence on rubber and the thermochemical evidence just mentioned, it is to be expected that, in general, molecules containing double bonds are likely to exhibit much greater deviations from the staggered bond positions than are saturated molecules[37]. This will not always be so, as is evident from the examples of β-gutta-percha and polychloroprene; presumably in these crystals the van der Waals' forces arising from the manner of packing of the molecules happen to favor the staggered position, whereas in rubber the packing is such that in some places the van der Waals' forces oppose the staggered configuration.

The nomenclature already described for saturated chains may also be used for chains containing double bonds, provided that additional information on the *cis* or *trans* configuration of the double-bonded unit is included. Thus β-gutta-percha (Figure 2 of Part I) is (*trans*) *BAC* or (*trans*) *CAB*, α-gutta-percha (Figure 5*a* of Part I) is (*trans*) *BAC* (*trans*) *CAB*, and the γ form of *trans* chain (Figure 5*b* of Part I) is (*trans*) *BAB* (*trans*) *CAC*. Rubber is (*cis*) *BAC* (*cis*) *BAC*. The other form of *cis* chain shown in this diagram is (*cis*) *BAC* (*cis*) *CAB*.

The discussion of ease of distortion and the magnitude of the potential barrier to rotation brings us to the question of molecular flexibility, and its connection with rubberlike properties. This topic will be taken up in Part III of this work, but meanwhile it may be remarked that molecules containing double bonds in the chain are likely to be more flexible (other things, such as side-chain hindrances to rotation, being equal) than saturated molecules, simply because the potential barrier to rotation around the single bonds due to the orienting tendency of the bonds themselves is lower when double bonds are present in the chain than in saturated chains; and therefore, if we accept in a general way the idea that rubberlike properties are likely to be shown only by substances having very flexible molecules, then this constitutes a special reason why polymers having double bonds in their chains are likely to have rubberlike properties. Perhaps this is why so many 1:4 polymers of butadiene derivatives, both natural and synthetic, have rubberlike properties—simply because every fourth chain bond is a double bond. To go any further it is necessary to consider both the preferred bond positions (and the potential barriers associated with them) and the effect of side groups in increasing or decreasing the heights of the barriers to rotation. This will be done in Part III.

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MOLECULAR STRUCTURE AND RUBBER-LIKE ELASTICITY

III. MOLECULAR MOVEMENTS IN RUBBERLIKE POLYMERS *

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In Part I of this work[1], the crystal structures of β-gutta-percha, rubber and polychloroprene (deduced from x-ray diffraction photographs) were described. In pursuance of the idea that rubberlike properties are due to molecular flexibility which result from the swivelling of the chain units around single chain bonds, it is necessary to consider which chain-bond positions are the most stable and what hindrances there are to rotation away from these positions. The question of the most stable bond positions was considered in Part II[2]. I now consider the evidence for the occurrence of rotation in rubberlike substances, the hindrances to rotation in different molecules, their effect on the crystallization or melting temperature, and the explanation of the mechanical properties of these substances in terms of structure and molecular movement, both above and below the crystallization temperature.

Rubber is noncrystalline and elastic at room temperature; but on cooling below 0° C it crystallizes[3], and in that condition has the mechanical properties of gutta-percha[4]; *i.e.*, a frozen specimen no longer has enormous elasticity, but it can be drawn or rolled out irreversibly, whereby the crystals become oriented. Conversely, if gutta-percha is warmed to 70° C, it becomes amorphous (transparent, optically isotropic and noncrystalline), and its mechanical properties are then like those of rubber—it is soft and elastic[5]. The difference between the two substances thus appears to be essentially a difference of crystallization temperature. These crystallization temperatures are remarkably low; *e.g.*, polyethylene, $(-CH_2-CH_2-)_n$, of comparable molecular length, crystallizes at 115-125° C. In attempting to understand rubberlike elasticity in terms of molecular behavior, the first question is why are the crystallization points of such enormous molecules so low, and why is the crystallization point of the *cis*-form of polyisoprene (rubber) lower than that of the *trans*-form (gutta-percha).

THE CRYSTALLIZATION POINTS OF LONG-CHAIN POLYMERS

When a crystalline solid is heated, it melts when the amplitude of the thermal motions of the atoms, ions or molecules of which it is composed becomes great enough to destroy the regular arrangement in the crystals. The Lindemann equation[6] embodies the assumption that melting occurs when the amplitude of vibration of the structural units becomes equal to the distances between these units, and for a few metallic elements and simple salts it has been shown[7] that this equation leads to vibration frequencies in agreement with those calculated in other ways (from specific heats, "reststrahlen", and compressibilities). Similar

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calculations for molecular crystals have not been made, but it is certain that their melting points are determined by some such condition; the general rise in melting point with the molecular weight of organic molecules testifies to this, since the amplitude of vibration of a molecule at a given temperature must decrease with rising molecular weight. But this is valid only for rigid molecules; when one part of a molecule can make large movements with respect to another part, the mass of the moving parts, which controls the melting point, is not the mass of the whole molecule but that of comparatively rigid portions of the molecule, which move with respect to each other. Crystals composed of very flexible molecules are expected to have melting points much lower than those composed of rigid molecules of the same weight.

The molecules of long-chain polymers with which we are concerned consist of fairly rigid units joined by single bonds around which rotation can occur relatively easily. For instance, in a rubber molecule each isoprene unit,

$$-CH_2-C(CH_3)=CH-CH_2-,$$

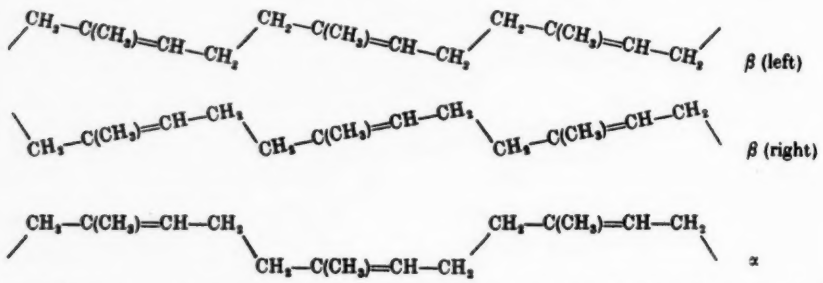
is relatively rigid, owing to the presence of the double bond, but rotation can occur around the single bonds which join the isoprene units together. In crystals of chain polymers, the molecules are packed together like a bundle of rods; vibrations perpendicular to the rods are likely to be very much larger than those along the rods, and it is therefore the former which cause melting when their amplitude reaches the required magnitude. The fact that the melting point of polyethylene is practically independent of the molecular weight when the latter is above 10,000[8] is in agreement with this concept. These lateral movements may be due partly to distortion of the bond angles, and partly to rotation around the single bonds; in some polymer molecules, rotation around the single bonds through large angles may occur—for example, through about 120° to alternative bond positions, or even through 360°; the amplitude of movement occurring in this way is far greater than that likely to result from bond-angle distortion, and therefore ease of rotation around the single bonds is likely to be the main influence which determines the melting point, at any rate in hydrocarbon polymers, in which the intermolecular forces are comparatively weak. The melting points of crystals composed of molecules in which rotation is easy are likely to be many degrees lower than those composed of molecules in which rotation does not occur.

First of all, evidence will be presented which leaves no doubt that major changes of molecular configuration due to rotation around the single bonds do occur in gutta-percha and polychloroprene at the crystallization point.

EVIDENCE ON MOLECULAR MOVEMENTS AT THE CRYSTALLIZATION POINT

Gutta-percha at 70° C is amorphous. On cooling, it may crystallize in two different forms, known as α (formed on slow cooling) and β (formed on rapid cooling). These two forms are not simply different arrangements of the same molecules, but have different chain structures; the identity periods of the chains (4.7 A.U. for the β form produced by rapid cooling, 8.9 A.U. for the α form produced by slow cooling) leave no doubt of this. The difference between the two chains is simply a difference in position of the single bonds

(CH_2-CH_2) which join the (*trans*) isoprene units together[1]. The two types of molecules are illustrated in Figures 2 and 5*a*[1]; they may be represented thus:



(Each isoprene unit is, as far as its carbon atoms are concerned, approximately planar, the plane being perpendicular to the paper; the connecting links—CH_2—CH_2 bonds—lie nearly in the plane of the paper.)

Evidently, the single bonds which determine the molecular configuration switch over spontaneously from one position to another in the amorphous substance.

That the change of molecular configuration occurs at the moment when a molecule takes its place in a crystal is confirmed by the fact that in any one β crystal the molecules are all either left-handed or right-handed, not mixed. For, suppose β molecules were formed previous to crystallization; the probability of formation is the same for left-handed as for right-handed molecules; hence in any group of molecules we should expect to find equal numbers of the two types, and when the group crystallized we should get an arrangement containing equal numbers of left- and right-handed molecules. (It is very unlikely that, in a nonfluid medium, the molecules would be able to sort themselves out into separate groups of thousands of left-handed molecules and thousands of right-handed molecules. Limited movements, necessary to convert a random grouping into an ordered arrangement, must occur, but extensive migrations of large numbers of molecules are unlikely.) It is thus necessary to assume that, at the moment of crystallization, each molecule assumes whichever configuration is necessary for convenient packing with other surrounding molecules. Evidently, the most stable mode of packing is one in which all the molecules in one crystal have the same configuration and, accordingly, molecules change their configuration as required. Conversely, when a crystal melts, bond oscillation sets in at the melting point. The same argument with regard to change of configuration of β-type molecules applies to polychloroprene, which is structurally analogous to β-gutta-percha. For rubber itself we have no evidence on the type of molecular movement which occurs, since its crystal structure happens to include both left- and right-handed molecules; it is, however, reasonable to suppose that in rubber the type of molecular movement is similar to that in polychloroprene and gutta-percha at or above their melting points, since the molecules of all these substances are built on the same principles (see Part I).

Free rotation around simple bonds is, of course, a well-known phenomenon in liquids and solutions, and the concept has been much used in recent theories of the structure of rubberlike polymers; but the evidence now presented is the first direct evidence that such rotation does occur spontaneously in rubberlike polymers. The term free rotation is perhaps a little misleading, as it suggests rotation at uniform speed, or quite random rotatory movements. Actually, in

all probability, there is a rapid switching of the bonds from one definite position to another, as in ethane and its derivatives[2]. This is probably what happens in the rubberlike polymers discussed here; the CH_2-CH_2 chain bonds are continually oscillating from one definite position to the other. When this happens in a long-chain polymer molecule, it means that the whole molecule is spontaneously wriggling; an attempt to suggest this is made in Figure 1, in which the molecules are represented in skeletal fashion to avoid confusion. Two modes of wriggling, both consistent with the maintenance of essentially straight chains, are illustrated, but many other modes are possible. The movements may not be confined to oscillation between two positions; the third bond position allowed

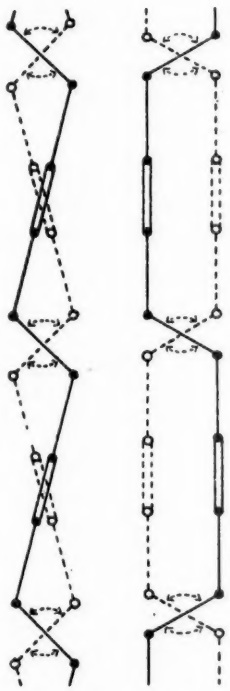


FIG. 1.—Gutta-percha molecules wriggling.

by the principle of staggered bonds[2] may also be visited; there is, however, no evidence on this point.

I now ask whether the onset of molecular wriggling is directly responsible for the melting of the crystals, or whether such wriggling can occur in the crystals. It is necessary to ask this question, because it appears that in certain crystals whole molecules rotate; in other words, the rotation of the molecules does not cause melting. Now molecular rotation at temperatures far below the melting point occurs only in crystals composed of molecules which are roughly spherical, *e.g.*, camphor derivatives, or disk-shaped[9]. These molecules can rotate without disturbing their neighbors unduly, and this is evidently the reason why the rotation of the molecules does not cause the crystals to melt. Among chain compounds it appears that, in some crystals of normal paraffins and alcohols, the

molecules rotate about their long axes (causing a phase change) a few degrees below the melting point[10]. Such molecules have roughly cylindrical symmetry; yet it appears that when a molecule, through its vibrations, pushes away its neighbors to an extent sufficient to permit complete rotation of the molecule, the amplitude of movement is nearly sufficient to melt the crystal; a further rise of temperature of only a few degrees is necessary to cause melting. Now the amplitude of movement in gutta-percha molecules which are wriggling in the manner described is much greater than that necessary for rotation of the roughly cylindrical molecules just mentioned. Hence, it seems reasonable to suppose that wriggling is not likely to occur in the crystals, but that the onset of molecular wriggling is directly responsible for the melting of the crystals. There is no evidence on the matter; the x-ray patterns which indicate a precise structure in the crystals[1] do not rule out the possibility of wriggling in the crystals, for changes of configuration might take only a small fraction of the time, and thus might not affect the x-ray patterns; but it certainly seems unlikely. At any rate, it will be assumed as a working hypothesis that the onset of molecular wriggling is responsible for the melting of the crystals.

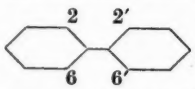
On this hypothesis, the principal reason why the crystallization temperatures of rubber and similar substances are so remarkably low is that rotation around the single bond is relatively easy (compared with polyethylene, for instance). Intramolecular forces are so free that the Van der Waals forces urging crystallization are balanced at a much lower temperature than that to be expected for more rigid molecules of similar size. In other words, each isoprene (or chloroprene) unit has a freedom of movement approaching that of monomeric isoprene or chloroprene; hence the crystallization points of polyisoprene and polychloroprene approach those of the small monomer molecules. Other effects which might influence the crystallization point are the packing difficulties of awkwardly shaped molecules; if molecules do not pack neatly, the van der Waals forces cannot play their full part. The crystal densities give some indication of the efficiency of packing; those of gutta-percha, rubber and polyethylene, calculated from the unit-cell dimensions of the crystals, are 1.04, 1.00 and 1.00, respectively; these are so similar that the influence of this factor on the crystallization point is likely to be quite subsidiary.

If accepted, the hypothesis that chain-bond oscillation (causing major changes of molecular configuration) is responsible for the melting of these rubberlike polymers leads to the inquiry why rotation around the single bonds occurs at a lower temperature in rubber and polychloroprene than in gutta-percha; and further, why the crystallization temperatures of all three substances are so much lower than that of polyethylene.

HINDERED ROTATION IN CHAIN POLYMERS

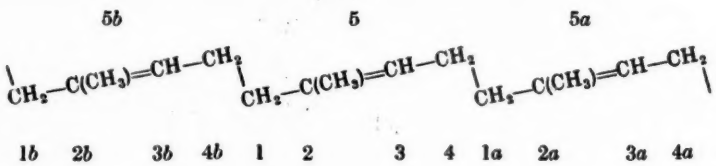
It will be assumed that the most stable positions for the bonds, and the energy required to move a bond from one position to another, are determined by two factors: the orienting tendency of the electron pairs forming the bonds, and the interactions of the atoms or groups held by the bonds. It has been suggested that the potential barrier to rotation in ethane and propane—some 3000 calories per methyl group—is due chiefly to the first of these factors, the orienting tendency of the bonds themselves[11]. It will be assumed, then, that in a saturated molecule, bond orientation alone is responsible for a barrier of this order of magnitude. Now in propylene, $CH_3-C\begin{matrix}\diagup\!\!\diagup CH_2\\ \diagdown H\end{matrix}$, and in acetone,

CH_3>C=O, the methyl groups rotate more easily; the barrier is 1000-2000 calories[12], apparently owing to the presence of the double bond. Presumably the same effects occur in chain-polymer molecules; when a double bond is present, as in rubber, gutta-percha and polychloroprene, rotation around the adjacent single bond is likely to occur more easily than in a comparable saturated molecule. This may be the reason why the melting points of these polymers which have double bonds in their chains are low.

The explanation of the differences between the three unsaturated polymers is to be sought in the other factor—the interactions of the groups held by the bonds. Evidence relevant to this question is available in the large volume of work which has been done on the racemization of diphenyl derivatives[13]. It appears that for these substances the predominant factor which controls ease of rotation around the single bond is the size of substituent groups in key positions. Thus, when fluorine atoms are present at the 2, 2′, 6 and 6′ positions of biphenyl, 

, racemization (due to rotation around the single bond) is so easy that resolution into optically active forms cannot be achieved, whereas if the larger chlorine atoms or methyl groups are present in these positions, resolution can be effected, and racemization does not occur in solution, even at 100° C. The polarity of groups in these positions, and the presence of substituents in other positions, have only secondary effects. Therefore, in considering ease of rotation in the three unsaturated polymers, I look for geometrical hindrances to rotation.

In gutta-percha, it is known that at the melting-point



the CH_2-CH_2 chain bonds (4*b*–1 and 4–1*a*) swing from one side of the isoprene unit to the other. The shortest route from one position to the other is illustrated in Figure 2; bond 1–4*b* swings (around bond 1–2 as axis) through about 120°. When this happens, carbon atom 4*b* has to pass within 2.6 A.U. of the methyl carbon atom 5; since the external radius of a CH_2 or a CH_3 group is 1.8–2.05 A.U., there will evidently be some hindrance to this rotation. (The sizes of the balls representing atoms in Figure 2 are arbitrary; actually the electron clouds are much larger, so much so that joined atoms overlap enormously. But to give the electron clouds their correct sizes would obscure the stereochemistry; therefore in the drawing the atoms are symbolized by small balls.) There is an alternative route involving rotation through 240° in the opposite direction, but this offers no advantages; atom 1*a* would have to pass within 2.5 A.U. of 5 and 1 within 2.5 A.U. of 5*b;* and, in addition, the wider sweep would be hindered by surrounding molecules. The shorter route involving rotation through 120° is therefore the more probable. It has been seen that this rotation is hindered by the size of the groups which have to pass each other, and at low temperatures no rotation

is possible; but with rise of temperature the vibrations of the atoms (involving bending and stretching of the bonds) increase, until a point is reached at which rotation can occur at certain phases of the vibrations. The thermal energy must be enough to overcome: (1) the small potential barrier due to preferred bond orientation; (2) the hindrance due to the size of the groups which have to pass each other, and (3) the hindrance due to other surrounding molecules. The temperature at which this occurs is about 60° C (actually 65° for the α form and 56° for the β form).

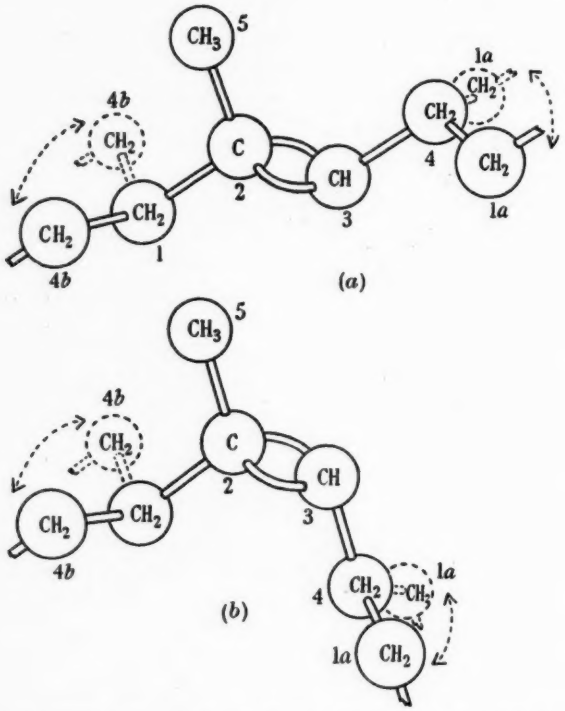


FIG. 2.—Bond oscillation in gutta-percha (above) and rubber (below).

The molecular structure of polychloroprene is entirely analogous to that of β-gutta-percha; it has a chlorine atom in place of the methyl group of gutta-percha. Now the distance between linked chlorine and carbon atoms (1.77 A.U.) is greater than the distance between linked carbon atoms (1.53 A.U.), and thus the chlorine atom of polychloroprene stands farther from the chain than the methyl group of gutta-percha; moreover, the external radius of chlorine atom appears to be slightly less than that of a methyl group. On both accounts the chlorine atom would be expected to offer less obstruction to chain-bond rotation than the methyl group (see Figure 2*a*). Chain-bond rotation, and thus molecular wriggling, could therefore occur at a lower temperature in polychloroprene than in gutta-percha. This may be the reason why the melting point of polychloroprene is lower than that of gutta-percha. There are other influences—the larger inertia of the chlorine atom, and the interaction of C–Cl dipoles—which might be expected to have the opposite effect and tend to increase the melting

point; but evidently such effects are secondary, possibly because melting can be achieved without moving the chlorine atoms at all; one can imagine the chloroprene units oscillating about the C–Cl bonds, so that the chains are wriggling (and the crystals melting) while the chlorine atoms remain stationary.

In rubber, as in gutta-percha, CH_2 group 4*b* (Figure 2*b*), in swinging around to the other side of the isoprene unit, has to get past the obstruction offered by the methyl side group. This methyl side group, however, is set slightly farther back (away from group 4*b*) in rubber than in gutta-percha. (In half the isoprene units in a rubber crystal, the angle $CH_3-C=CH$ is 115°; in gutta-percha the corresponding angle is 125°.) Furthermore, it can vibrate farther in the direction away from 4*b*. In gutta-percha, group 4, only 3.0 A.U. away at the other end of the double bond (Figure 2*a*), obstructs vibration in this direction, but in rubber (Figure 2*b*), owing to the *cis* double-bond configuration, no such obstruction is present, only a hydrogen atom being attached to C_3 on this side. Since vibration of the methyl group in the direction away from 4*b* is easier, group 4*b* can swing around past the methyl group at lower temperatures in rubber than in gutta-percha. This is evidently the reason why the crystallization point of rubber is lower than that of gutta-percha.

A qualitative explanation of the fact that rubber and polychloroprene are noncrystalline and elastic at lower temperatures than gutta-percha can thus be given on the basis of the simple stereochemical concept of geometrical hindrance to bond oscillation.

Comparison of these substances with saturated chain polymers is less simple, because there are two factors to be taken into account—the bond-orientation effect, as well as geometrical hindrance. To form some idea of the effect on the melting point of the higher bond-orientation barrier in saturated compared with unsaturated molecules, we need information on the melting points of saturated and unsaturated molecules in which the geometrical hindrances are the same. Rubber hydrochloride $(-CH_2-CH_2-CH_2-C(CH_3)Cl-)_n$ is being studied with this end in view. Meanwhile, in attempting to compare rubber and gutta-percha with polyethylene $(-CH_2-CH_2-)_n$, in addition to the difference in bond-orientation energies, there is another interesting difference. In rubber and gutta-percha, bond oscillation apparently sufficient to cause melting occurs between geometrically enantiomorphous, energetically equivalent positions (see Figure 2). But in polyethylene, the most stable form of chain is a plane zigzag, in which each chain bond is in a geometrically unique position; movement of a chain bond to either of the other two staggered positions is movement to a geometrically nonequivalent position of higher energy (higher owing to repulsion between the CH_2 groups[2]. This must increase the height of the energy barrier to be surmounted. (The magnitude of this effect is unknown; potential energy diagrams for *n*-butane, similar to those given for halogen derivatives of ethane[14], would give some idea of it, but such diagrams are not available.) Any increase in the height of the energy barrier would increase molecular rigidity, and therefore raise the melting point.

In polyethylene, the bond-orientation effect and the repulsion between the CH_2 groups coöperate in favor of the stability of the plane zigzag type of carbon chain, and the coöperation of the two factors is no doubt responsible for the high melting point. In some saturated polymer molecules having large substituent groups close together along the chain, it may happen that the two factors are in opposition: if mutual repulsion of the substituent groups opposes the staggered configuration preferred by the bonds themselves, it may

well happen that the energy barrier to rotation is reduced, and may even be negligible. This is probably why polyisobutylene, $(-CH_2-C(CH_3)_2-)_n$, with its pairs of methyl groups on alternate carbon atoms[15], has a low melting point, being amorphous and rubberlike at room temperature: examination of models of this molecule shows that, no matter what chain structure is assumed, mutual repulsion between the methyl groups opposes the staggered configuration; that is to say, the bonds prefer one configuration (with the bonds staggered); the methyl side groups prefer another. The net result is that all configurations have much the same energy, the barriers to rotation are small and the melting point is low.

Thus it seems possible to understand, in a rough general way, the melting points of long-chain polymers on the basis of the two hypotheses assumed in the foregoing discussion. These hypotheses are: (1) that melting is due to lateral movements of segments of more or less flexible molecules, and (2) that the energy required for rotation around the single bonds (the chief basis of molecular flexibility) is made up of two factors—the bond-orientation energy, and the interaction of the atoms or groups held by the bonds.

STRUCTURE OF AMORPHOUS RUBBER

I shall accept the conclusion that in amorphous gutta-percha, polychloroprene, and by analogy in rubber and other similar substances above their crystallization point, molecular wriggling (by which is meant spontaneous major change of molecular configuration of the type previously discussed) occurs spontaneously. I now inquire to what extent this leads to curling of the molecules. It should be noted that the low melting points of these substances can be adequately explained without assuming any curling at all; one can quite well imagine the molecules wriggling sufficiently to cause melting and yet retaining the straight chain structure found in the crystals (see Figure 1). It has, however, been pointed out by Mark[16] and others that, in the case of an isolated molecule, the very fact that the number of different curled configurations is much greater than the number of straight configurations must tend to favor an average curled configuration; in other words, each isolated molecule, owing to thermal movements, assumes a random configuration, the probability of an approximation to a straight configuration being very small. The question is to what extent these statistical effects operate in rubberlike substances, in which the molecules, far from being isolated, are packed close together. The x-ray pattern of amorphous rubber does not determine whether the molecules are or are not curled[17].

A theory of rubberlike elasticity was built, chiefly by Mark[16] and Kuhn[18], on the two assumptions that rotation around the single bonds is quite free, and that the molecules behave as if in isolation. The second assumption seemed from the outset improbable; however, a calculation by Kuhn[18] of the modulus of elasticity of rubber gave an approximately correct figure. This seemed encouraging support for the theory; but it has since been shown by Bresler and Frenkel[19] that if the existence of an appreciable barrier to rotation is taken into account, such calculations give moduli much smaller than the experimental values; a barrier of 3600 calories leads to a modulus of elasticity one-twentieth the experimental value. (It must be pointed out that the figure of 3600 calories for the height of the barrier to rotation, although possibly of the right order of magnitude, is not necessarily correct for rubber. Bresler and Frenkel's procedure was to consider the chain $(-CH_2-CH_2-)_n$ and assume that the barrier has the magnitude 3600 calories found for propane; actually, the value for

propane (where a methyl group rotates but does not move as a whole in relation to the rest of the molecule) is not appropriate for the long CH_2 chain, for which the barrier for *n*-butane (not yet known) would be more nearly correct, since in this molecule a whole CH_3 group swings around, and this would be comparable to the CH_2 group in the long chain. But, apart from this, the choice of the simple CH_2 chain as an example—a practice followed in most theoretical discussions—is an unfortunate one, for polyethylene is not a typical rubberlike substance; it is crystalline up to 115-125° C, and above the melting-point is a very viscous liquid. The magnitude of the barrier for rubber is unknown, but it is certainly not zero, and Bresler and Frenkel's calculations[19] show that the existence of a barrier of appreciable magnitude leads to a considerable reduction in the value of the modulus, calculated by Kuhn's method[18]. This must mean that Kuhn's second assumption—that the molecules behave as if in isolation—is not justified; the correct result of his calculation was the fortuitous outcome of making two incorrect assumptions which happened to have roughly equal and opposite effects on the result.

I conclude, therefore, that intermolecular action in rubberlike substances is by no means negligible. Its effect on the form and packing of the molecules naturally depends on the nature of the substance (the geometry of the molecules and the forces between individual atoms); but we may form some idea of the general effect of such forces by referring to the structures of ordinary liquids composed of small molecules. It appears that, in such substances, disorder is not complete; there is, especially just above the melting point, some attempt at an orderly arrangement, the type of arrangement being usually a rough approximation to that which exists in the crystal of the substance in question. In other words, although the molecules are moving about, they are more often than not surrounded by neighboring molecules arranged in roughly the same manner as they are in the crystal[20]. For molecules of roughly spherical shape, this tendency is greatest for polar liquids, such as water, and least for nonpolar liquids, such as hydrocarbons; the shape of the molecules plays an important part only when there is considerable departure from spherical shape[21]. In long-chain polymers the most extreme departure from spherical shape occurs; consequently one expects to find, in these substances just above their melting points, partially ordered arrangements of molecules corresponding roughly with the arrangements found in the crystals. In all crystals of long-chain polymers, as far as is known, the molecules are arranged parallel to each other as in a bundle of rods. Any other arrangement would give very poor packing and a low density. But the molecules are much larger than the crystals and, therefore, any one molecule in the course of its length passes through several crystals[22]. I therefore visualize a structure of the type shown in Figure 3*a*, in which crystals (groups of straight parallel lines representing molecules) are tied together by molecules, each of which passes through a number of crystals. It is this feature which is responsible for the cohesion and high tensile strength of long-chain polymers compared with molecular crystals composed of small molecules. Just above the melting point, therefore, one should find that portions of molecules are associated in roughly parallel groups, as in Figure 3*c*, in which the wavy lines represent molecules wriggling in the way described previously. This arrangement differs from that in the crystal, in that the molecules are not precisely parallel (one can imagine them pulled away from parallel positions by the tying portions of molecules) and are not arranged side by side in a regular way. With rise of temperature, the arrangement should become more and more disordered, and the molecular configuration more irregular.

I now inquire whether the size of the semiordered regions which exist just above the melting point is at all comparable with that of the crystals which exist below the melting point. Judging from the breadth of the diffraction spots, the crystals in the polymers mentioned in this paper are at least several hundred A.U. across, *i.e.*, there are straight portions of molecules several hundred atoms long packed together in thousands to form precise arrangements. On this question, comparison of the extensibilities of crystalline and rubberlike polymers is instructive.

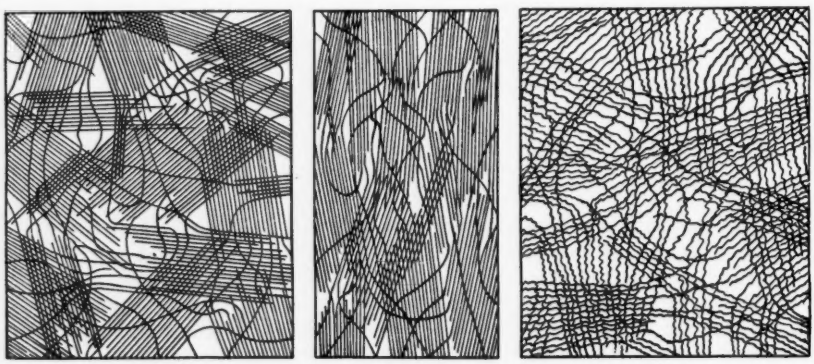


FIG. 3.—(*a*) Crystalline long-chain polymer. Lines represent molecules, groups of parallel straight lines represent crystals. (*b*) The same cold-drawn. Crystals apparently parallel. (*c*) Amorphous rubberlike polymer. Wavy lines represent wriggling molecules. When rubber is frozen, the fine structure becomes like *a*; when it is stretched, the fine structure becomes like *b*.

MECHANICAL PROPERTIES ABOVE AND BELOW THE MELTING POINT

It is worth noting, first of all, that the concept of molecular wriggling gives an immediately convincing reason for the characteristic semiliquid properties of rubberlike substances—their softness, flexibility, and ease and rapidity of extension and contraction. These substances have such properties simply because the spontaneous thermal movements of segments of molecules are of similar magnitude to the movements of whole molecules in ordinary liquids, from which rubberlike substances differ in their lack of fluidity which is obviously due to the enormous length of the molecules and the resultant entangling effects. Thermal movements of such magnitude are really implied in the statistical theory of Mark and Kuhn, and in the treatment of Meyer[23]; but such movements have not received the attention they deserve. For instance, in the statistical theory emphasis has always been placed on the concept of irregular molecular configuration in unstretched rubber, rather than on spontaneous changes of configuration; and when Meyer[24] speaks of rubberlike substances as being "liquid in two dimensions and solid in the third", he is referring to the forces between different molecules and between parts of the same molecule, rather than to molecular movements. The present point of view is that neither irregularity of configuration nor any particular distribution of intermolecular forces is sufficient to confer rubberlike properties. There are many amorphous polymers, especially interpolymers, in which the molecules probably have an irregular configuration, but they will not be rubberlike unless the molecules are so flexible that the thermal motions of segments of molecules cause spontaneous major changes of configuration.

As regards extensibility, it seems at first sight that there is a fundamental difference between rubberlike and crystalline specimens. The latter, *e.g.*, polyethylene, gutta-percha and rubber hydrochloride at room temperature, can be drawn out to 3-5 times their original length, but when drawn, they remain extended with the crystals all nearly parallel to each other (Figure 3*b*); rubber, polychloroprene and polyisobutylene can be stretched 7-10 times their original length and, when released, contract spontaneously. It is found, however, that cold-drawn crystalline polymers, when warmed to temperatures a little below their melting points, contract spontaneously and almost completely[25]. The fact that contraction occurs when the specimens are still largely crystalline shows that a structure composed of crystalline blocks joined by tie molecules can have a reversible extensibility of at any rate 400 per cent. The difference between this behavior and that of rubberlike substances is one only of degree, and this suggests that the dimensions of the molecular bundles in rubberlike substances at room temperature may be not very different from those of the crystals formed below the melting point.

In the extension and contraction of crystalline polymers, the tying portions of molecules must play the most important part; the statistical effects considered by Mark, operating on the tying portions of molecules, are no doubt responsible for the spontaneous contraction just below the melting point. The crystals presumably remain, for the most part, as organized units; but it must often happen that, in cold-drawing, different parts of the same crystal are dragged in different directions, and the crystal will then be sheared along cleavage planes. That this actually happens in polyethylene is shown by the fact that when orientation in a cold-drawn specimen is particularly good, the crystal size is smaller than in the original undrawn specimen, as shown by the breadth of x-ray diffractions. Similarly, in spontaneous contraction just below the melting point, there is x-ray evidence that the size of the crystals increases; small crystals evidently join together to form larger ones. These facts all help us to understand what happens when a rubberlike substance is stretched. First of all, the molecular bundles can be figured as being pulled by the tying portions of molecules into approximately parallel orientation; but slipping of individual molecules and shearing of molecular bundles into two or more groups occur very much more easily than in a crystalline polymer, owing to the spontaneous wriggling of the molecules. (If a molecule gets into a jam when in one configuration, it may be able to get past easily when in another configuration.) There is consequently much more slipping and changing from one molecular bundle to another than there is in crystalline polymers; to this may be ascribed not only the far greater ease of extension, but also the greater extensibility of rubberlike polymers compared with crystalline polymers.

CRYSTALLIZATION BY STRETCHING

During the stretching of rubber, crystals are formed and the structure of fully stretched rubber is analogous to that of cold-drawn crystalline polymers (Figure 3*b*). Crystallization has usually been attributed to the straightening out of curled molecules, which, when they find themselves parallel to each other, are able to form a precise arrangement; but there is another effect which may be of equal or greater importance. If a tangle of string is pulled out as if it were a piece of rubber, not only do many of the strands become roughly parallel to the direction of pulling, but also it is obvious that many strands are laterally compressed by surrounding strands. Therefore, in stretched rubber, not only are

the bundles of molecules roughly parallel, but many of them are in a state of lateral compression. The molecules are forced closer together laterally, and are obliged to take up less space; the obvious way of taking up less space laterally is to stop wriggling and pack together neatly; this the molecules do, forming crystals. The greater the extension, the greater the proportion of molecular bundles laterally compressed and, therefore, the greater the proportion of crystals.

It is necessary to mention that, although the properties of gutta-percha above its melting point (65° C) are in general similar to those of rubber at room temperature, it does not crystallize on stretching[3]. The reason for this is probably that gutta-percha molecules are considerably shorter than rubber molecules; there is more internal irreversible slipping, as is shown by the fact that stretched amorphous gutta-percha on release does not return to its original dimensions. Consequently it is not possible to get sufficient tension on the specimen to cause crystallization at 70° C.

In mechanical properties, the greatest contrast between rubberlike and crystalline polymers is shown by the behavior of stretched specimens on release. Polyethylene and gutta-percha at room temperature remain extended (except for a small contraction of 10 per cent) and crystalline, while rubber contracts spontaneously and almost completely and becomes amorphous. The reason why the former substances remain extended is that, during stretching, the crystals are to some extent pulled to pieces and put together again in a different way. On release, the statistical effects to which Mark has drawn attention tend to make the tying portions of molecules assume a random configuration; this would disorient the crystals and thus cause contraction to the original length. But contraction cannot go very far unless the jammed-in crystals can be pulled to pieces by shearing along cleavage planes; the pull of the tie molecules is not sufficient to achieve this, and the specimen therefore remains extended except for a small contraction of 10 per cent. Near the melting point, shearing becomes easier and the increased thermal motions of the tie molecules are sufficient to pull the crystals to pieces, and spontaneous contraction occurs. In contrast, when stretched (largely crystalline) rubber is released, a small initial contraction leads to a slight relaxation of lateral compression; the crystals now have more room, and molecules on the surfaces of some crystals start wriggling. This loosening of the structure then permits further contraction; more molecules then wriggle, and the process spreads through the whole specimen, until the melting of the crystals and the contraction of the specimen is complete. The rapidity of contraction (snap) is due to the fact that wriggling molecules slip past each other almost as easily as the molecules in an ordinary liquid.

A reasonable general account of the mechanical properties of crystalline and rubberlike polymers and the relation of these types to each other can thus be given on the basis of the concepts developed in the foregoing discussion.

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THE COURSE AND MECHANISM OF AUTOÖXIDATION REACTIONS IN OLEFINIC AND POLYOLEFINIC SUBSTANCES, INCLUDING RUBBER *

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The tendency of olefins to absorb molecular oxygen increases rapidly with increase in unsaturation. In monoolefins absorption is usually very slow unless it is actively promoted by irradiation, by the use of temperatures above room-temperature, or by chemical catalysts; in dienes and trienes it usually becomes considerable in diffused daylight; and in higher polyenes it tends to occur unpreventibly and excessively. The strong tendency towards oxidation shown by polyenes appears to be shared by unconjugated and conjugated substances alike, although the precise courses of reaction are probably somewhat different in the two cases. In the present paper attention is focussed mainly on monoolefinic and unconjugated polyolefinic substances.

THE PRIMARY AUTOÖXIDATION REACTION

Although in the autoöxidation of many different olefinic substances little peroxidic substance survives at the end of reaction, there is no reason to doubt that the first stage in every such autoöxidation is the formation of peroxide groups. Rubber hydrocarbon, for example, after vigorous autoöxidation, involving high oxygen intake, gives a product containing only traces of peroxidic substance, but when the oxidation is conducted cautiously, the bulk of the ingoing oxygen (80 per cent or more) is found in the early stages of reaction to be in peroxide form. It has usually been assumed, following the Engler-Bach hypothesis, that the oxygen is absorbed molecule by molecule, and adds at the olefinic centres, so that the primary reaction is, in fact, held to be a simple additive reaction: $-CH=CH- + O_2 \rightarrow -\underset{\displaystyle O}{\overset{\displaystyle |}{CH}}-\underset{\displaystyle O}{\overset{\displaystyle |}{CH}}-$. This view cannot be maintained: the disappearance of olefinic unsaturation rarely keeps pace with the incorporation of oxygen although, under usual conditions of reaction, severe diminution of unsaturation due to secondary reactions often occurs. In all the unconjugated olefinic systems examined by the authors, oxygen appears to enter at the methylenic carbon atoms in the α-positions to the double bonds, and hydroperoxide groups are formed:

$$-CH_2-CH=CH- + O_2 \rightarrow -CH(OOH)-CH=CH-.$$

Each hydroperoxide group thus formed contains one atom of active oxygen and one atom of active hydrogen, but the introduction of the group leaves the olefinic unsaturation intact.

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INTRINSIC STABILITY OF HYDROPEROXIDES

All hydroperoxides decompose comparatively readily, but some are sufficiently stable to make it possible to isolate them in tolerably pure form. The hydroperoxides of cyclohexene, 1-methylcyclohexene, 1,2-dimethylcyclohexene and methyl oleate can thus be obtained by fractionally distilling the autoöxidation product at reduced pressure, but with most polyolefins decomposition of the $-OOH$ groups takes place unavoidably side by side with their formation, so, after the early stages of oxygen absorption, secondary reaction products begin to accumulate, and thus no pure hydroperoxide or polyhydroperoxide can be isolated in quantity. The polyisoprene, *e.g.*, dihydromyrcene,

$H(CH_2-CMe=CH-CH_2)_2H$, and rubber, $(-CH_2-CMe=CH-CH_2-)_n$,

and doubtless the drying-oil acids, *e.g.*, linoleic acid:

$$C_5H_{11}-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H,$$

and linolenic acid:

$$C_2H_5-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H,$$

as well as the unconjugated polyprene fish-oil acids, *e.g.*, eicosatetraenoic acid and docosahexaenoic acid[1], all belong to the latter category. In the fish-oil acids the intake of oxygen (in peroxidic form) in diffused daylight at room temperature is astonishingly rapid, but decay is rapid also.

CONDITIONS OF HYDROPEROXIDE-FORMATION AND DECAY

Absorption of oxygen is promoted by sunlight or ultraviolet light and by numerous chemical catalysts, both organic and inorganic; within the limits of present observation absorption is usually facilitated by raising the reaction temperature above room temperature. The decomposition of $-OOH$ groups is strongly promoted by elevated temperatures apparently also by prolonged illumination, and by certain chemical catalysts such as iron salts, which can play a dual role as peroxidation promoters and peroxide destroyers. For the successful photochemical preparation of hydroperoxides in quantity, experience indicates that it is advisable to curtail the duration of oxidation by operating with good illumination at the highest temperature which the instrinsic stability of the particular peroxide will allow.

POINT OF ENTRY OF HYDROPEROXIDE GROUPS. INDUCTIVE EFFECTS

Experiments have indicated (*cf.* preceding paper) that inductive influences in olefinic chains have an important effect, both in facilitating reaction, and in determining the seat of reaction (*e.g.*, as between C_α and C_δ) in systems such as $-C_\alpha H-\overset{\overset{CH_3}{\downarrow}}{C_\beta}=C_\gamma-C_\delta H-$, even though the structural and experimental conditions which are most favorable to autoöxidation are not such as to point to a reaction mechanism of ionic type. Thus, although any methylene group (less easily a CH_3- or $>CH$-group) which is adjacent to an ethylene bond is a potential seat of reaction, autoöxidation appears in practice more likely to occur at C_α in the system above rather than at C_δ. The most complete evidence of the effectiveness of alkyl groups in determining the seat of reaction is seen

in the oxidizing action of selenium dioxide in the presence of acetic acid[2], where oxidation occurs preferentially at the precise points to be expected on the basis of the inductive influences present. Thus in the following systems[3], attack occurs first at the points marked *:

$$\overset{*}{C}H_3-CMe=CHMe, \quad CH_3=\overset{*}{C}H_2-CMe=CH_2, \quad \overset{*}{C}H_3-CPr=CHMe,$$

$$\overset{*}{C}H_3-CMe=CHEt,$$

$$CH_3-\overset{*}{C}H_2-CPh=CHMe, \quad CH_3-\overset{*}{C}H_2-CH=CHMe,$$

$$\overset{*}{C}H_2R-CEt=CH-CH_2R.$$

In the case of polyisoprene hydrocarbons, including rubber, present information indicates that peroxidation occurs not only at C_α in the system $C_\alpha-C_\beta=C_\gamma-C_\delta$, but extensively at C_δ also. In all the polyene drying-oil acids, peroxidation seems to occur with exceptional facility at methylene groups situated between double bonds, just as ionic reactivity is very great in the methylene groups of the system $-CO-CH_2-CO-$ and $-CH=CH-CH_2-CO-$.

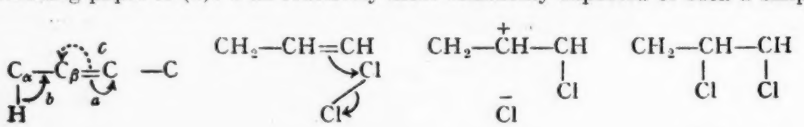
There are, however, other peroxidizable substances besides olefins, *e.g.*, dialkyl ethers[4] and chloroform[5], in which inductive influences seem to be potent. Thus the inductive influence of oxygen in the *n*-dialkyl ethers, and in di-isopropyl ether: $R-CH[H] \rightarrow OR \longrightarrow R-CH[OOH]-OEt$, as also that of chlorine in chloroform: $Cl_3 \rightarrow C[H] \longrightarrow CCl_3-OOH$, doubtless renders oxidation easier than it is in saturated hydrocarbons, where usually high temperatures, catalysts, or irradiation are necessary to make a hydrogen atom detachable and, in consequence, attack by molecular oxygen possible of initiation. Where, however, the structure of a substance and the ionizing capacity of the medium in which it is placed favor ionic dissociation of hydrogen, the course of autoöxidation may not involve the formation of an organic hydroperoxide at all. Thus in the case of α-ketols, α-aminoketones and α-methoxyketones, autoöxidized in presence of alkali, the reaction probably consists purely in the oxidation by molecular oxygen of the enolic anion derived from the ketol, etc.[6], *i. e.*, in an oxidation-reduction change, for example:

$$-C(\bar{O})=C(\bar{O})-+O_2 \rightarrow -CO-CO-+\bar{O}-\bar{O} \rightarrow 2-CO\bar{O}.$$

MECHANISM OF PEROXIDATION

(*a*) Relation of Substitution to Addition in Olefins

The system responsible for the varied substitutive reactions described in the preceding paper is (I). The reactivity most commonly expected of such a simple



(I) (II) (III) (IV)

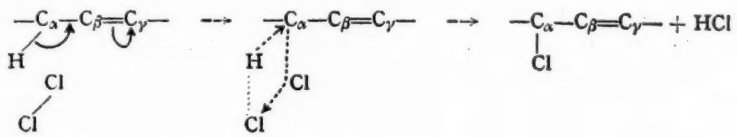
olefinic system is addition at the double bond. The activating polarization *a* and creates at C_γ a point of relatively high electron density, so electrophilic reagents, whether positive as in the case of HCl or incipiently positive as in Cl_2, are enabled to attack the system there, and reaction proceeds through the

well-known stages, as shown for Cl_2 addition in (II)-(IV). The normal mechanism of olefinic addition is thus an ionic one and, according to the usual electronic principles, an alkyl group attached to system (I) and C_β assists by its inductive action the polarization *a* at the expense of the alternative *c*, and so both facilitates additive reaction and influences the direction of addition at the double bond. But it is clear from the examples quoted in the preceding paper that the system (I) possesses in addition to its additive properties a marked tendency to undergo substitution at C_α (or C_δ), and the mechanism of this substitutive reactivity is of considerable interest and practical importance.

Lability of a methylenic hydrogen atom is normally to be expected in the systems:

$$-CH[H]-C=O, \quad -CH[H]-CH=CH-C=O,$$
$$-CH[H]-CH=CH-CH=CH-C=O, \text{ etc.},$$

provided a basic catalyst (usually $-OH$ or $-OEt$ ions) is present to detach the hydrogen as proton. Also in the reinforced (conjugated) olefinic systems present in cyclopentadiene, fluorene, diphenylmethane, etc., detachment of a hydrogen atom from the α-methylene group is possible, provided a basic catalyst is present to remove it as an ion. But in the three-carbon system, $-CH_2-CH=CH-$, as it occurs in an olefin, ionic separation of methylenic hydrogen in the absence both of a basic reagent and of an ionizing medium is ordinarily unknown[7] and not to be expected. Therefore to explain the substitutive halogenation of an olefin by chlorine or bromine on an ionic basis, it would be necessary to envisage a reaction similar to that of aromatic substitution, in spite of the fact that the characteristic nuclear structure is absent:



In its form, however, the α-methylenic substitution in question resembles side-chain substitution rather than nuclear substitution, and hence a radical type of mechanism is to be expected; also there is no obvious reason why an electrophilic reagent should attack the olefin preferentially at C_α, thus enforcing substitution, when a point of higher electron density (C_γ) is available. It is not surprising, therefore, that substitutional halogenation has proved to depend on radical formation rather than on a bimolecular reaction. In the case of the peroxidation of olefins, the general efficacy of light and of radical-producing catalysts, etc., in promoting reaction, and the ease with which peroxidation occurs in olefins (in nonpolar media) point to the same conclusion.

As noted above, evidence available at present suggests that inductive effects due to alkyl groups attached to the ethylenic carbons of olefins assist substitutive as well as additive reaction, and serve to determine the point of substitutive as well as of additive attack; also there is some experimental indication that this holds for peroxidation reactions[8]. If, then, separation of hydrogen in the substitutive reaction is not ionic, the conclusion must be drawn that the inductive effects are able to assist the symmetrical (free-radical) separation of the electron pair in the methylenic C—H bond, and it is common experience that such separation is promoted by nonionizing rather than ionizing media. Waters[9] has

pointed out that internal inductive effects in complex molecules produce great changes in the electrostatic bond-energy, and also that the probability that bond-fission processes at a bond A—B will take the unsymmetrical course

$$A-B \rightarrow A^{+}+B^{-}$$

(to yield two ions) and not the symmetrical course $A-B \rightarrow A^{\cdot}+B^{\cdot}$ (to yield two neutral radicals) becomes greater as the ionic resonance energy of the bond increases. The ionic character then of a bond such as C—H, which has only low resonance energy, is likely to be considerably inferior to the free-radical character. Waters points out further that the electrostatic energy needed to create a single gaseous ion is greater than the thermal energy needed to dissociate a covalent bond into two neutral radicals, but the dielectric effect of a solvent in reducing the energy of ion formation is very great. Hence it appears that at least those α-methylenic substitution reactions which are conducted in the undiluted hydrocarbon or in media of low dielectric constant are likely to be based on symmetrical dissociation of the C—H bond; furthermore it is to be inferred that the C=O group in the system —CH—C=O enhances the tendency to ionic dissociation rather than radical dissociation of the adjacent C—H bond, since otherwise it is surprising that autoöxidation in oleic and similar acids and esters occurs at the CH_2-groups in α-position to the ethylenic double bonds, and not at those adjacent to the carboxyl groups.

Now, although when olefins are submitted to the action of chlorine or bromine they show both the additive and the substitutive reaction under suitable experimental conditions, the evidence is not yet clear whether a corresponding additive reaction can be achieved when oxygen is the reagent. Certain cyclic conjugated dienes, but not so far as is known open-chain ones, can add oxygen terminally[10], but here, presumably, owing to the paramagnetic character of the oxygen, and the easily assumed free-radical phase of the diene, the addition is not ionic, but of radical type:

$$(\cdot C{-}C{=}C{-}C\cdot + \cdot OO\cdot \rightarrow -C(-O{-}O){-}C{=}C{-}C-),$$

and this being so, the possibility of achieving successful monomeric additive reaction in a monoölefin will depend on the ability of the ethylenic carbons to assume, in presence of the reagent, the radical form and to make two simultaneous or nearly simultaneous links with oxygen:

$$(-C{=}C- + \cdot OO\cdot \rightarrow \cdot C{-}C\cdot OO\cdot \rightarrow C(-O{-}O)-C),$$

either of which courses is, for steric reasons, hardly likely to be easily accomplished. There is as yet no clear evidence that this additive peroxidation has ever been achieved, but with respect to the general possibility of forming peroxides additively from monoölefins, three cases may be cited: (1) certain olefins which contain no α-methylene group, and notably *as*-diphenylethylene[11], appear to be capable of giving under illumination polymeric peroxides:

$$-E{-}OO{-}E{-}OO{-}E{-}OO- \quad (E=Ph_2C_2H_2),$$

presumably formed by polymerization of the monomer $-E-OO-$[12], (2) other similar olefins, *e.g.* styrene[13], give with oxygen polymers of the olefin which con-

tain but little peroxidic oxygen, and (3) certain olefins add oxygen readily after they have first been attacked by halogen atoms[14], *e.g.*,

$$[2\ CH_2{=}CH{-}CH_2Br \xrightarrow{Br\cdot} 2\ CH_2Br{-}\dot{C}H{-}CH_2Br \xrightarrow{O_2} (CH_2Br)_2CH{-}OO{-}CH(CH_2Br)$$

With regard to the relative ease of radical attack at the α-methylene group and at the double bond, recent experiments[15] indicate that in cyclohexene phenyl and benzoate radicals (from dibenzoyl peroxide) attack most successfully at the methylene group.

(*b*) Photoperoxidation

Both oxygen and peroxides especially the latter, have been found by Kharasch and his coworkers[16] to be generally efficacious in starting reaction-chains in hydrogen halide additions, presumably owing to the assistance which the paramagnetic character of the former and the radical-yielding, or possibly the coördinative power, of the latter lend to the formation of halide atoms:

$$(HX + \cdot OO\cdot \rightarrow HOO\cdot + X\cdot;\ R\cdot + HX \rightarrow RH + X\cdot).$$

In view of the remarkable ease with which, in the absence of inhibitors, peroxidation succeeds in diffused light in the case of rubber and drying oils, in comparison with the comparative immunity of monoölefins from oxidative attack, it seems at first sight that the feature which predisposes towards oxidation is the inherent structural lability of the hydrogen atoms, which is at its maximum in α-methylenic groups. In polyolefins, the appropriate atoms might then be considered to be labile enough to permit their being detached by oxygen sufficiently readily and frequently to start enough reaction chains to sustain a reasonably rapid rate of oxidation. Such a process might be expected to be initiated more easily by introduction of a little already-formed peroxidic substance (probably providing radicals) than by oxygen alone. The course of reaction would then be:

$$-CH{-}C{=}C- + \cdot OO\cdot \text{ (or } R\cdot) \rightarrow -\dot{C}{-}C{=}C- + \cdot OOH \text{ (or RH)}$$

$$-\dot{C}{-}C{=}C- + \cdot OO\cdot \rightarrow -\underset{\displaystyle OO\cdot}{\overset{|}{C}}{-}C{=}C-$$

$$-\underset{\displaystyle OO\cdot}{\overset{|}{C}}{-}C{=}C- + -CH{-}C{=}C- \rightarrow -\underset{\displaystyle OOH}{\overset{|}{C}}{-}C{=}C- + -\dot{C}{-}C{=}C-$$

and the role of such catalysts as cobalt and copper salts in initiating reaction could be represented thus:

$$-CH{-}C{=}C- + Cu^{++} \rightarrow -\dot{C}{-}C{=}C- + Cu^{+} + H^{+}.$$

But Morgan and Naunton[17] have found that the rate of thermal oxidation of rubber in the early stages of reaction is independent of oxygen pressure, confirming earlier results of Williams and Neal[18], and thus indicating that a course of reaction dependent on bimolecular collision between oxygen and the hydrocarbon is unlikely. They suggest that the autoöxidation of rubber involves a chain mechanism, and they advance the scheme:

$$R \rightleftharpoons R^*;\ R^* + O_2 \rightarrow RO_2^*;\ RO_2^* + R \rightarrow RO_2 + R^*;\ RO_2^* \rightarrow RO_2.$$

where R* is an activated rubber double bond, RO_2* a rubber peroxide, and RO_2 the product of rubber oxidation. This scheme is difficult to reconcile with the experimental findings cited above respecting the unsaturated peroxidic character of the rubber photoöxidation products first formed, since reaction is made dependent on acceptance of the double bond as the necessary point of initiation and the subsequent seat of peroxidation; also the rubber peroxide seems to be regarded as having only a transient existence. An alternative to both of the foregoing schemes is that initiation of peroxidation depends on previous dissociation of the olefin at the α-methylenic C–H bond:

$$(\text{—CH—C=C—} \rightarrow \text{—}\dot{\text{C}}\text{—C=C—} + \text{H}\cdot)$$

under the influence of light. No direct evidence can, however, be advanced for this course of reaction. The kinetics of olefinic autoöxidation are at present the subject of examination.

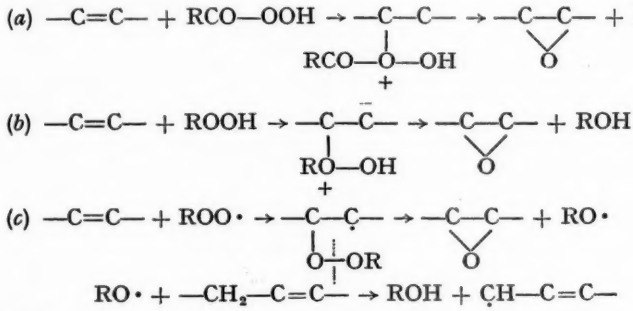
Somewhat similar problems arise with regard to the polymeric addition of sulfur dioxide to olefins, and the polymeric peroxidation of olefins. Here reaction would superficially appear to begin as the result of bimolecular interaction between oxygen and olefin, in contrast to the oxygen- or peroxide-induced abnormal addition of HBr to olefins, in which the attack of the oxygen catalyst or peroxide catalyst is directed to the additive reagent. Whether in the polymerization reactions, the first-step necessarily takes place at a methylene group and never at a double bond is not clear.

SECONDARY AUTOÖXIDATION REACTIONS

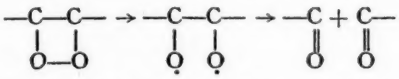
Except with the most stable hydroperoxides, and then only under optimum conditions of operation, peroxide decay occurs side by side with new peroxidation. Thus in polyenes—especially long-chain polyenes, such as rubber—hydroperoxide groups and their oxygeno derivatives inevitably occur in the same molecule. This mixing of peroxidic and secondary groupings is aided by the usual very uneven distribution of oxidative attack over the olefinic molecules present. The principal, and doubtless the most invariable, feature of secondary autoöxidative changes is that the hydroperoxide groups themselves revert to hydroxyl groups, in some circumstances to keto groups, and concurrently the active oxygen is consumed in oxidizing either the adjacent or some remote double bond—the latter perhaps in another molecule. This oxidative action may proceed as far as chain scission at the double bonds, or may oxygenate and so saturate the double bonds without severing them. Chain-scission reactions can occur with embarrassing facility in rubber after even slight oxygenation; in a less serious degree they occur unavoidably in polyene fish-oil acids and shorter polyisoprenes. It is impossible at present to distinguish between thermal and photochemical secondary decompositions. The basic reactions, so far as they are at present known, seem to be the following.

1. Interaction of a hydroperoxide group with a double bond, giving a hydroxyl group at the former and an epoxy group at the latter. This reaction is in part comparable to the action of an organic peracid at an ethylenic bond (Equation *a*), and since it can be brought about at will by heating an olefin hydroperoxide with an olefin, may be represented as in (*b*). But since the change appears to occur with greater facility during the actual autoöxidation reaction than subsequently by thermal decomposition of the isolated hydroperoxide, it possibly is brought about during the autoöxidation in a more direct way, *e.g.*,

by interaction of a radical peroxide with a double bond, as shown in (*c*). This reaction is of intermolecular type, occurring between a peroxide group in one molecule and either a double bond in another molecule, or a remote double bond in the same molecule.

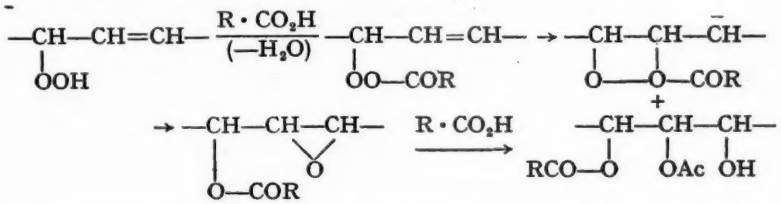


2. Scission of the carbon chain at the double bond occurs with considerable ease, both during the autoöxidation reaction, *i.e.*, perhaps as the result of irradiation, and subsequently by thermal decomposition. The precise mechanism of this change in either case remains still to be determined. There is insufficient evidence at present for rejecting finally the possibility that, in some very small degree, scission can occur during the original autoöxidation by momentary formation and immediate decomposition of a cyclic peroxide, thus:



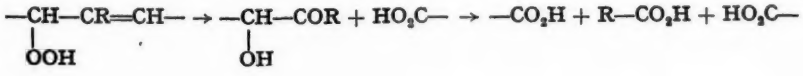
but this mechanism cannot apply to thermal decompositions of the hydroperoxide.

3. In the presence of organic acids or their anhydrides, autoöxidation occurs readily. This may be represented for the free acid:



4. By decomposition of the hydroperoxide in presence of mineral acid, a reaction analogous to the foregoing and yielding a saturated triol, $-CH(OH)-CH(OH)-CH(OH)-$, occurs.

5. Subsidiary scission can occur between an ethylenic bond and an α-carbon atom:



6. Polymerization occurs by the interaction of $-OOH$ groups and double bonds. This appears to give mainly dimerides of ether type, possibly to be represented as involving the reaction:
In addition, radical forms, RO·, produced by thermal or possibly photochemical

$$-C=C- + HOO-R \rightarrow -C(-)-C(H)-\overset{+}{O}-OR \rightarrow -C(OR)-C(OH).$$

dissociation of the hydroperoxides, and radical forms, ROO·, produced in the primary peroxidation reaction, probably take part in the process by reacting with other olefinic systems present.

7. In the presence of iron salts, and in some cases as the result of spontaneous or violent thermal decomposition, hydroperoxides give unsaturated ketones. This is comparable to the spontaneous formation of esters from the peroxides of ethers: $RCH(OOH)-OR' \rightarrow RCO-OR' + H_2O$.

8. In the presence of alkalies, extensive hydrolysis of the hydroperoxide groups occurs: $ROOH + H_2O \rightarrow ROH + H_2O_2$, with concomitant oxidative degradation of the double bonds by the hydrogen peroxide liberated.

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α-METHYLENIC REACTIVITY IN OLEFINIC AND POLYOLEFINIC SYSTEMS *

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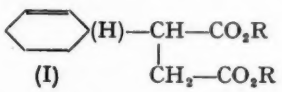
The most important reactions of olefins and olefinic systems have usually been considered to be additive ones. Recent work, however, has shown that substitutive reactions are likely to prove of equal importance, and attention is here drawn to a variety of substitutions which occur at the α-methylene groups of olefinic systems. Doubtless the reaction mechanisms of these processes differ from example to example, and it is of very considerable importance in respect to the utilization of olefins, rubber, and drying oils the exact nature of these mechanisms should be determined. Of particular interest is the influence on α-methylenic substitution of (1) reaction conditions and (2) alkyl substitution at the ethylenic carbon atoms. When chlorine reacts with an olefin in a polar solvent, the halogen acts as an electrophilic reagent and the olefin as electron donor, so an ionic process of addition takes place; when, however, the reaction occurs in the gas phase, or in solvents of low polarity, it takes a more complicated course, involving chain processes and radical intermediates[1]. Also, in additions of ionic character, the presence of alkyl substituents on the ethylenic carbon atoms is well known to facilitate additive reactions, and to influence the direction of addition of reagents: it appears to do the same in α-methylenic substitutions, including (so far as present evidence gives an indication) even reactions which are fairly certainly radical reactions. Certain of the substitutions described below are liquid-phase reactions, which apparently proceed quite independently of photochemical activation, and in these especially, the relationship of substitution to addition in terms of the intrinsic reactivity of the system $-CH_2-CH=CH-$ needs to be defined.

THE MALEIC ANHYDRIDE REACTION

Maleic anhydride combines readily with conjugated dienes (Diels-Alder reaction) in hydrocarbon media, in spite of the lessened unsaturation and greater activation energy of the ethylenic bonds due to resonance in the diene system; yet it will not similarly unite with monoölefins or unconjugated polyolefins. This, together with the conclusion of Wassermann that, for diene synthesis to be successful, two-point contacts at the correct positions must be made by the colliding reactant molecules, suggests that reaction involves the radical form, $\cdot CH-CH=CH-CH\cdot$, of the diene. Reactions between olefins or unconjugated polyolefins and maleic anhydride (or maleic esters) can, however, be promoted[2], provided an elevated temperature is used. Thus cyclohexene, 1-methylcyclohexene, dihydromyrcene and rubber unite above 220° with methyl or butyl maleate. The reaction is a substitution at the α-methylene groups of the olefin, giving in the case of cyclohexene first (I), and then a disubstitution product which is



(I)

probably mainly cyclohexene-3:6-disuccinic ester. The reaction proceeds with

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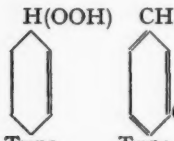
particular ease in the system $-CH=CH-CH_2-CH=CH-CH_2-$ of drying oils, and the system $-CH_2-CMe=CH-CH_2-$ of rubber, and succeeds also if analogs of the maleic compounds, *e.g.*, ethyl cinnamate, are used. What appears to be an anlogous reaction occurs at moderate temperatures (around 100°) between the same reactants if a little peroxide is added as reaction starter.

PEROXIDATION REACTIONS

With little doubt, peroxidation constitutes the first step in all autoöxidations of olefins, although many or all of the peroxide groups formed may undergo decomposition before the end of reaction. The absorbed oxygen forms hydroperoxide groups which are attached substitutionally at the methylene groups adjacent to the olefinic double bonds; the point of entry at one α-methylene group or another seems to be greatly influenced by alkyl substituents in the carbon chain. It has been found that cyclohexene[3], 1-methyl-cyclohexene, 1,2-dimethylcylcohexene[4] and tetralin[5] give relatively stable peroxides of type I by



Type I

Type II

$CH_2(OOH)-CMe=CH-CH_2-CH(OOH)-CMe=CH-CH_3$ Type III

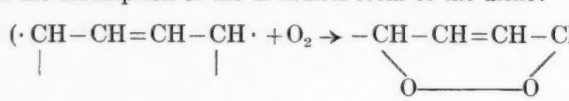
$CH_3-(CH_2)_6-CH(OOH)-CH=CH-(CH_2)_7-CO_2Me$ Type IV

$CH_3-(CH_2)_7-CH=CH-CH(OOH)-(CH_2)_6-CO_2Me$ Type V

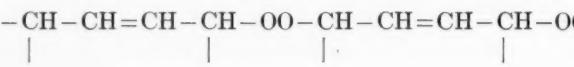
absorption of oxygen (without solvent) in ultraviolet light, whereas *m*- and *p*-xylene[6] and cymene[7] give hydroperoxides by substitution in the side chain (type II). Dihydromyrcene[8] gives relatively unstable mono- and dihydroperoxides by substitution at one or other of the α-methylene groups in the chain (type III), while rubber[9] and other polyisoprenes[4] behave quite similarly, giving lightly or heavily peroxidized (multihydroperoxidic) substances. Oleic acid[10] gives a mixture of relatively stable mono- and di-peroxides in which the hydroperoxide groups are found at C_8 or C_{11} (types IV and V) or at both.

In all these hydroperoxidic autoöxidation products, the original double bonds remain intact, except in so far as the peroxidic groups have undergone secondary decomposition, involving utilization of their active oxygen for attack at the unsaturated centres. Such secondary decomposition proceeds side by side with peroxidation, and is often well-nigh impossible to arrest; where this occurs isolation of pure polyhydroperoxides is impossible.

The foregoing remarks apply to mono- and unconjugated polyolefins. In the case of cyclic conjugated dienes, such as terpinene, 2,4-cholestadiene, ergosterol, dehydroergosterol, anthracene, rubrene, etc.[11], terminal addition of molecular oxygen seems to be possible, and this is probably dependent (as in the Diels-Alder reaction) on the assumption of the di-radical form of the diene:



Some conjugated dienes, however, are reported to give polymolecular peroxides,



FREE RADICAL ATTACK ON OLEFINS: VULCANIZATION BY DIBENZOYL PEROXIDE

Dibenzoyl peroxide readily reacts with saturated and aromatic hydrocarbons, with alcohols, organic acids, etc., at temperatures above 100°. The peroxide decomposes thermally to give Ph· and Ph−CO−O· radicals[13], and these are able to attack an organic substance RH, with formation of new compounds and new free radicals:

(1) $Ph\cdot + RH \rightarrow PhR + H\cdot$
(2) $Ph\cdot + RH \rightarrow PhH + R\cdot$
(3) $Ph-CO-O\cdot + RH \rightarrow Ph-CO-OR + H\cdot$
(4) $Ph-CO-O\cdot + RH \rightarrow Ph-CO_2H + R\cdot$
(5) $R\cdot + RH \rightarrow R-R + H\cdot$, etc., etc.

The new free radicals are available for further attack on the molecules present or, if their concentration permits, for intercombination. The fate of the various radicals formed must depend largely on the reaction conditions, since, if the reactant RH is present in very large excess, the intercombination of free radicals must mainly give place to their attack on RH; therefore potentially, at any rate, the action of the decomposing dibenzoyl peroxide is twofold, comprising a substituting agency (reactions 1 and 3) and a molecule-linking or "polymerizing" agency (reaction 5).

This action is seen when RH is cyclohexene, taken in large excess, so that the chance of encounter of phenyl or benzoate radicals from the peroxide with cyclohexene molecules will be great, and that of their encounter with other free radicals will be small. Since cyclohexene has two likely points of attack, *viz.*, the α-methylene groups and the double bonds, it may be expected, if P represents either a phenyl or a benzoate radical derived from the peroxide, that the following types of reaction will occur:

(*a*) $C_6H_{10} + P\cdot \rightarrow PH + C_6H_9\cdot$ or $C_6H_9-P+H\cdot$
(*b*) $C_6H_{10} + C_6H_9\cdot \rightarrow C_6H_9-C_6H_9 + H\cdot$,

and also, by attack of the radicals at the olefinic double bonds:

(*c*) $C_6H_{10} + P\cdot \rightarrow P-C_6H_{10}\cdot$
(*d*) $C_6H_{10} + P-C_6H_{10}\cdot \rightarrow C_6H_9-C_6H_{10}-P+H\cdot$, or $P-C_6H_{11}+C_6H_9\cdot$
(*e*) $C_6H_{10} + P-C_6H_{10}\cdot \rightarrow P-C_6H_{10}-C_6H_{10}\cdot$, etc., etc.

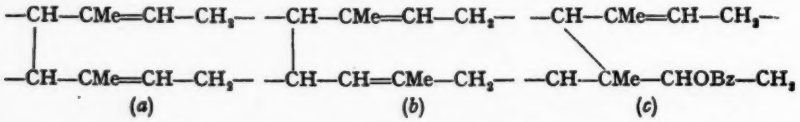
The products actually found are numerous[14], but all agree with expectation according to the above scheme. Attack by the radicals at the α-methylene groups greatly exceeds their attack at the double bond, and molecule-linking is almost entirely confined to two-molecule linkings.

The vulcanization of rubber by dibenzoyl peroxide at 140° was thought by its discoverer[15] to be substantially represented by the equation:

$$(C_5H_8)_n + n\,Ph-CO-OO-CO-Ph \rightarrow n\,Ph-CO_2H + (C_5H_7-O-CO-Ph)_n.$$

Conformably with this view, the unsaturation of the product is stated to be but little diminished[16], but on the analogy of the cyclohexene reactions, and, bearing in mind the labilizing action of the methyl groups in the rubber chain on the hydrogen atoms of adjacent methylene groups, the two processes of molecule-linking and substitution may be expected to give vulcanizates in which the rubber chains are extensively substituted at the α-methylene groups by

benzoate and (to a lesser extent) by phenyl groups and, at the same time, are in some degree cross-linked by bonds (intermolecular or intramolecular) joining the methylene groups of different rubber units, *e.g.*, as shown in *a* and *b*, or bonds joining α-methylene groups to double bonds, as exemplified in *c*:



Vulcanization by dibenzoyl peroxide is, therefore, likely to be mainly a combination of cross-linking and substitution of the rubber chains, as distinct from cross-linking and double-bond addition, as in sulfur vulcanization.

REACTION OF QUINONES

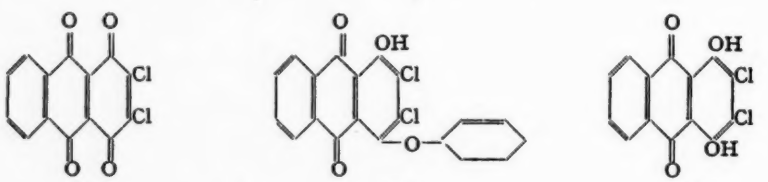
In the maleic anhydride reaction described above, there is no tendency for three-carbon residues ($-CH-CH=CH-$) and hydrogen atoms formed by dissociation of the olefin to unite at the oxygen terminals of the system:

$$O=C-CH=CH-C=O,$$

present in the anhydride—possibly for lack of the resonance form:

$$\cdot O-C=CH-CH=C-O\cdot$$

Successful reaction in this case depends on activation of the ethylenic bond of the anhydride. In the case of quinones the situation is different, and when the quinone is suitably substituted, *e.g.*, in the chlorodiquinone (A), reaction at the terminals of the system, $OC-CH=CH-CO$, can be realized by heating the



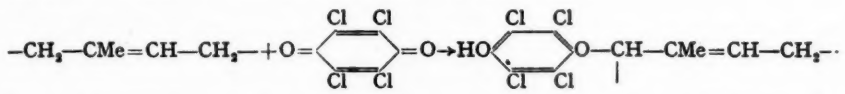
quinone with an olefin, such as cyclohexene or tetralin[17]. In this way the hydroquinone (B) from cyclohexene, or an analogous compound from tetralin, is formed. At a higher temperature these hydroquinones of type (B) break down, giving cyclohexadiene (or 1,2-dihydronaphthalene) and the hydroquinone (C), so that the net result of the reaction carried out at high temperature is dehydrogenation of the olefin and reduction of the quinone.

Various halogenated quinones react with rubber, causing a species of vulcanization[18] (inferior for practical purposes to sulfur vulcanization). Tetrachloroquinone (chloranil) is particularly successful, a part of it (stated to be one-half) becoming reduced to the corresponding hydroquinone as a result. Since the latter can be reoxidized to the quinone by including among the reactants a proportion of a suitable oxidizing agent, *e.g.*, PbO or HgO, the vulcanizing agent can apparently function repeatedly. Although Ostromislensky

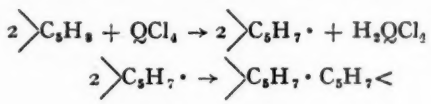
has suggested that a complicated reaction occurs between the chloroquinone and the C_5H_8rubber units, thus:

$$2QCl_4 + 3C_5H_8 \rightarrow H_2QCl_4 + C_5H_7 - QCl_2 - C_5H_7 + C_5H_8Cl_2 \quad (Q = C_6O_2),$$

the true course of reaction probably involves the process:



Since chloranil is now known to be a particularly effective dehydrogenating agent[19] for hydroaromatic compounds, some degree of dehydrogenation similar to that brought about by the above-mentioned diquinone may well enter into the rubber-chloranil reaction. The production of conjugated diene units in this way may well facilitate some cyclization or some true polymerization of the rubber molecules, and so contribute to the vulcanized character. There is, however, the possibility that the quinone may serve to a greater or lesser extent as an oxidation-reduction system, and so lead to a more direct radical-linking of the rubber chains:



VESTERBURG REACTION

The earliest dehydrogenations of hydroaromatic substances were carried out by heating them with sulfur, whereupon hydrogen was removed as hydrogen sulfide. In the dehydrogenation of cyclohexene, however, no cyclohexenyl mercaptan (comparable with cyclohexenyl hydroperoxide) is to be found in the reaction mixture: instead, the hydrogen sulfide generated adds, as would be expected[20], to unused cyclohexen to give cyclohexyl mercaptan and to some extent dicyclohexyl sulfide[21]. It appears, therefore, that the formation of an unsaturated mercaptan by a reaction exactly analogous to that cited above between Criegee's diquinone and cyclohexene represents no essential stage in dehydrogenation by sulfur; instead, sulfur can probably function as hydrogen-acceptor by a direct mechanism.

SULFUR VULCANIZATION

When the Vesterburg reaction is applied to rubber at about 140°, ordinary sulfur-vulcanization ensues. This process has two main features: (1) the remarkable change in the physical properties (especially the solubility) of the rubber, and (2) the incorporation of sulfur in the rubber. Most authors have regarded the former as due to increase in the size of the rubber molecules arising from some kind of polymerization promoted by sulfur, and the latter as due to addition of sulfur at the double bonds. It has most often been concluded that the chief function of sulfur in the vulcanization process is to promote the formation of intermolecular links, usually considered to be sulfur bridges of one kind or another (sulfide, disulfide), but possibly to some extent direct C–C bonds. The desirable physical properties of the sulfur vulcanisates are deemed to depend on the cross-linked structure.

Two points have now become fairly clear, experimentally: (1) that the desirable physical properties of the vulcanizates are conferred before any seri-

ous diminution in unsaturation of the rubber has occurred, or any large proportion of sulfur has become chemically combined[22], and (2) that after this stage, which is presumably the essential vulcanizing or cross-linking stage, has been reached, chemical incorporation of sulfur sets in seriously and is attended by progressive decrease in unsaturation[23]. In view of the fact that sulfur is not ordinarily an additive reagent for olefinic double bonds, it is probably legitimate to deduce from (1) that the cross-linking essential to vulcanization, whether this is by direct C–C links or by sulfur bridges, probably affects primarily and mainly the α-methylene groups, and from (2) that the extensive incorporation of sulfur at the later stages of sulfur-vulcanization is a secondary process dependent on the attack at the methylene groups.

PHOTOGELLING OF RUBBER

The photogelling of rubber dissolved in a mixture of carbon tetrachloride and acetone, or in various other halogenated solvents, with or without added ketones, and with or without added peroxide or oxygen as sensitizing agents, has been described by Stevens[24]. Gelling proceeds fairly rapidly in sunlight, and the intensity and duration of illumination affect very greatly the physical character of the gels. The process is found to involve the extensive chemical incorporation of fragments of the solvents in the rubber, and doubtless it also involves cross-linking of the rubber molecules or units; it appears to resemble closely the action of dibenzoyl peroxide on rubber, save that the free-radicals responsible for the interlinking of molecules and the attachment of organic fragments to the rubber chains are derived from the solvents by photochemical decomposition.

HALOGENATION REACTIONS

The importance of α-methylenic reactivity is very evident in halogenation reactions. The results of Groll, Hearne *et al.*[25], following earlier results of Stewart *et al.*[26], and Deanesly[27], with respect to olefins, and of McGavack[28] with respect to rubber, have shown that, under certain circumstances, α-methylenic substitution partly or wholly replaces double bond addition. There is often a second-order substitution at the ethylenic carbons.

Both substitution and addition occur when an olefin in gaseous form is mixed with chlorine at low or nonelevated temperatures. For substitution to become easy, however, and to complete successfully with addition, the lability of the α-methylenic hydrogen atoms requires enhancing, either by structural modification of the normal olefinic chain or by using high temperatures. If an alkyl group is present at one of the ethylenic carbons of the normal chain, as in $-\underset{a}{CH_2}-\underset{b}{CMe}=\underset{c}{CH}-\underset{d}{CH_2}-$, the substitutive capacity at *a* (or at *a* and *d*) is greatly increased, and some small degree of substitution occurs also at *c*. If a higher alkyl group than methyl is employed, the ease of substitution seems to be increased, and evidence indicates that, in the system $R_1R_2C=CR_3R_4$, the well-known rules regarding the inductive efficiency of alkyl groups in promoting and directing the course of ionic addition reactions are valid here also[29]. The substitutive reaction is found to be a liquid-phase reaction, occurring in liquid films on the walls of the vessel, and proceeds at about the ordinary pressure (low or moderate temperature) in the absence of light, and without other catalyst

than the walls of the vessel. At a suitable rate of gas flow, isbutylene (1 mol.) gives with chlorine (1 mol.):

(*a*)		(*b*)		(*c*)[30]		(*d*)	
$CH_2Cl-CMe=CH_2$	+	$CH_3-CMe=CHCl$	+	CMe_3Cl	+	$CH_3-CMeCl-CH_2Cl$	+
0.87 mol.		0.03 mol.		0.01 mol.		0.06 mol.	
				Satd. dichlorides	+	trichlorides	
				0.02 mol.		0.01 mol.	

and the ratio of the percentage yield of (*a*) to that of (*b*) changes little with varying conditions from approximately 97/3. Tertiary amylene,

$$CMe_2=CHMe+CH_2=CMeEt,$$

gives comparable results.

For the promotion of a good degree of substitutive halogenation in normal-chained olefins, it is necessary to rely on the provision of suitable experimental conditions. High temperatures (300°-600°, according to the olefin and halogen concerned) are effective, and propylene gives at 600°-650° at least 85.5 per cent of chloropropenes which comprise $CH_2Cl-CH=CH_2$ (96 per cent),

$$CH-CCl=CH_2 \text{ (3 per cent) and } CH_3-CH=CHCl \text{ (1 per cent).}$$

When bromine is used to react with propylene, the substitutive tendency is even more marked for, although at 200° addition predominates, at 300° the product consists of substitutively formed monobromides; moreover, at either temperature the substitutive tendency is more pronounced with bromine than with chlorine. The temperature which must be reached before addition gives place to substitution is higher for ethylene than for unbranched alkylethylenes, and very much higher for ethylene than for branched olefins.

The chlorinations which occur at elevated temperatures, whether substitutive or additive, appear to be mainly (not exclusively) of radical character, and the incidence of the specific reaction chains is very dependent on the experimental conditions[31]. The role of oxygen during chlorination is unexpected in that, whereas small concentrations of oxygen catalyze strongly the substitutive reaction, especially at higher temperatures, considerable concentrations of oxygen suppress both reactions below 300°; above 300° the addition which occurs in presence of oxygen is probably of gas-phase, bimolecular type. Radicals containing an ethylenic linkage seem to be more stable to oxygen than those which have only single C–C bonds.

LEAD TETRACETATE REACTIONS

Criegee[32] found that lead tetracetate reacts directly with cyclohexene to give not only 1,2-diacetoxylcyclohexane but mono- and diacetoxylcyclohexenes. This means that acetoxyl groups add at the double bond of the olefin, and also substitute one or both of the α-methylene groups to give 3-, 3,6- and 3,3-derivatives. Since both the substitutive and additive reactions consist in transfer of acetoxyl groups from reagent to olefin, it appears that reaction is of free-radical rather than ionic type, in spite of the fact that reaction is sometimes conveniently conducted in presence of glacial acetic acid (to arrest hydrolysis of the reagent). The essential reaction is then the thermal decomposition:

$$Pb(OAc)_4 \rightarrow Pb(OAc)_2+2AcO\cdot,$$

the acetoxyl radicals thus formed attacking the double bond or an α-methylene group of the olefin, as in the dibenzoyl peroxide reaction above. It is of interest that further acetoxyl radical attack can occur, as perhaps might be anticipated, at the CH_3 groups of ingoing acetoxyl groups, to give $\cdot O-CO-CH_2-OAc$. Lead tetrabenzoate, tetrapropionate, etc., serve in place of the acetate, the ingoing benzoyloxy groups from the former not being subject to subsidiary attack by $Ph-CO-O\cdot$ radicals.

SELENIUM DIOXIDE REACTIONS

Selenium dioxide behaves with extraordinary regularity in attacking olefins, aldehydes and ketones at the α-methylene groups. As indicated in the succeeding paper, the point of attack in the case of olefins is very precisely determined by alkyl substitution in the chain. The reaction is carried out by heating the olefin or carbonyl compound with powdered selenium dioxide, whereupon the methylene groups attacked are oxidized to carbonyl groups, unless the reaction is carried out in presence of a fat acid, in which case the fat acid ester of the corresponding alcohol is obtained ($>CH_2 \xrightarrow[AcOH]{SeO_2} >CH\cdot OAc$). The reaction strongly resembles autoöxidation, and can be applied to the oxidation of the alkyl groups of alkylaromatic compounds; the condition of the reagent is not without importance, old samples having been found to favor formation of bimolecular, *e.g.*, ketol, reaction products[33]. The exact course of the reaction, which does not appear to be normally of ionic type, is as yet undetermined.

OZONIZED OXYGEN REACTIONS

Oxidative attack at α-methylene groups by ozonized oxygen has been reported to occur in α-pinene[34], α-hydrindene[35], and dodecahydrophenanthrene[36], and seems, from the nature of the decomposition products, to occur to a minor extent in rubber[37]. Possibly this attack ought to be attributed to the oxygen of the reagent rather than to ozone, especially as ozone is reported[38] to catalyze oxidation by oxygen.

ATTACK BY OXIDIZING AGENTS

The hydrogen atoms of α-methylene groups which stand between two double bonds are especially labile, and it is not surprising to find that certain oxidizing agents, including perbenzoic acid[39] and chromic acid[40], are reported to attack these active groups in linoleic and linolenic acids and in cyclopentadiene, although they attack the double bonds in oleic, elaidic and ricinoleic acids. The character of the reactions and of the products is, however, unknown. The α-methylene groups in cyclohexene, 1-methylcyclohexene and in 6-dodecyne are oxidized to carbonyl by chromic acid[41].

THERMAL POLYMERIZATIONS OF OLEFINS

In many low-molecular polymerization processes among olefins, it has been assumed that hydrogen separates from an ethylenic carbon atom of one molecule and adds at the double bond of another. This assumption is unnecessary in low-molecular processes which are catalyzed by hydrion (*cf.* Whitmore's hypothesis), and probably also in most photochemical or radical-initiated polymerizations. In the case of purely thermal polymerizations of alkylethylenes, it seems not unlikely that dissociation of hydrogen *atoms* from the α-methylene

groups of some monomeric molecules leads in many examples to the addition of the residual hydrocarbon radicals, *e.g.*, $\dot{C}H-RCH=CHR'$, at the double bonds of other undissociated molecules, giving eventually low-molecular polymerides.

DOUBLE-BOND DISPLACEMENT

Hydrogen can be displaced as an ion from the α-methylene groups of olefinic chains when strong caustic alkali is used as reagent at a sufficiently high temperature. The conditions need to more drastic than are required for the α, β, β,γ-change in unsaturated acids. The possibility of such displacement was first shown by Moore[42] in the case of the unconjugated triene chain of linolenic acid, the product being a conjugated isomeride of linolenic acid.

The examples of methylene reactivity discussed briefly above are doubtless only representative instances, but they serve to show the considerable substitutive reactivity of olefinic systems, especially of polyolefinic substances such as rubber.

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IONIC AND RADICAL MECHANISMS IN OLEFINIC SYSTEMS, WITH SPECIAL REFERENCE TO PROCESSES OF DOUBLE-BOND DISPLACEMENT, VULCANIZATION AND PHOTOGELLING *

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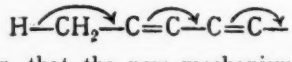
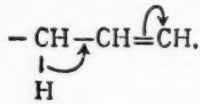
The α-methylenic reactions discussed in the preceding two papers recall a series of interesting observations by Baker and Nathan[1], which indicate that a *p*-methyl substituent attached to the benzene nucleus can permit electron release to the nucleus in a manner that appears only in lesser degree in higher alkyl groups, and may be absent in some (*e.g.*, Bu^{γ}). Thus in *p*-methylbenzyl bromide, the suggested function of the methyl group (dotted arrows in (I) per-

(I)

mits additional electron release at the C–Br bond, and so facilitates the anionization of the bromine. Baker and Nathan suggest that the electrons of the duplet constituting the C–H bond of the methyl group are less localized than those in a similarly placed C–C bond, and hence that a methyl group attached to the necessary conjugated unsaturated system is capable of electron-release by a mechanism similar to the tautomeric effect:



They make clear, however, that the new mechanism functions in addition to the generally accepted inductive (+I) effect of alkyl groups, and they find experimentally that the efficiency of representative alkyl groups is in the order: $Me > Et > Pr^{\beta} > Bu^{\gamma}$, and that the suggested electron release must be of mesomeric rather than of tautomeric type. The phenomenon noted by Baker and Nathan seems to be part of a much wider phenomenon which applies to unconjugated (as well as to conjugated) polyolefins, and even to monoölefins which contain the system, $-CH_2-CH=CH-$, and it appears likely that, in general, the three-carbon system exists in a mesomeric state corresponding to the electron shifts in



* Presented at a Discussion on "The Structure and Reactions of Rubber", held by The Faraday Society in London, May 29, 1942. Permission has been generously granted to reprint this paper in RUBBER CHEMISTRY AND TECHNOLOGY.

This conclusion has, if correct, certain consequences with respect to the ionic reactivity and physical properties of olefinic substances: these consequences are exemplified in the following two sections. In addition, however, the mesomeric condition as here conceived appears to lie at the root of the well known cracking rule of diene polymers (as it is illustrated in the cracking of rubber to isoprene, the reversal of the diene synthesis etc.), whereby the links which break, *i.e.*, the weakest links, are never the C—C links adjoining the double bonds

$$\left(\text{—}\vdots\text{—C—C = C—C}\vdots\text{—}\right);$$

also it appears to exert a marked influence on the tendency of the α-methylenic C—H bond to dissociate symmetrically. Such observations as have been made in the latter respect indicate that alkyl substituents attached to the ethylenic carbon atoms do, indeed, appear to facilitate symmetrical dissociation; nevertheless it is difficult at present to disentangle the purely inductive effect of the alkyl groups from the mesomeric effect in a system such as

$$R-\overset{*}{C}H_2-C(\overset{*}{C}H_3)=CH-\overset{*}{C}H_2-R',$$

characteristic of the polyisoprenes and rubber. The available evidence suggests that dissociative reaction does not occur principally at the methyl groups, but it is too fragmentary to distinguish quantitatively between the three C—H bonds marked *.

IONIC DOUBLE-BOND DISPLACEMENT

Double-bond displacement induced by the action of an alkali is well known under the name of three-carbon or prototropic change, and is a common property of α, β- or β,γ-unsaturated fat acids, ketones, nitriles, etc. The same type of change has been observed in the case of the aryl olefins, β-phenylpropylene, eugenol and Δ^2-dihydronaphthalene, in which the aryl group replaces >CO or —CN as an activating group but, until recently, was unknown in olefinic chains in which the double bond was remote from all activating groups of the usual types. Moore[3], however, found that linolenic acid,

$$C_2H_5-(CH=CH-CH_2)_3-(CH_2)_6-CO_2H,$$

when heated with alkali passed slowly into an isomeric conjugated form. Linoleic acid and linoleyl alcohol similarly pass into conjugated forms[4], and it is undoubtedly a common property of 1,4-diene hydrocarbon systems to pass with moderate facility into one or both of the forms $-CH=CH-CH=CH-CH_2-$ and $-CH_2-CH=CH-CH=CH-$ when the substances containing them are heated with caustic alkali at elevated temperatures. The question then arises as to whether displacement also occurs in the 1,5-diene system,

$$-CH=CH-CH_2-CH_2-CH=CH-,$$

or generally in monoölefinic systems, $-CH_2-CH=CH-CH_2-$, in which the double bond is remote from carbonyl or similar activating groups.

In the case of the 1,5-diene system as it is represented by the linked isoprene units $-CH_2-CMe=CH-CH_2-$ of squalene, dihydromyrcene and rubber, prolonged treatment with an alkali, under conditions which are successful with linolenic and lineoleic acids, has been found to cause no recognizable degree of

bond shift[5]. With regard to the simple monoölefinic system, there is on record the early statement of Varrentrapp[6] the oleic acid, when fused with caustic alkali, gave a considerable yield of palmitic and acetic acids, as if by hydrolytic fission of Δ^2-octadecenoic acid:

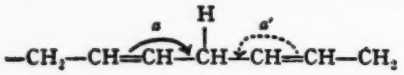
$$C_8H_{17}-CH=CH-(CH_2)_7-CO_2H \longrightarrow [C_8H_{17}-(CH_2)_7-CH=CH-CO_2H] \longrightarrow C_{15}H_{31}-CO_2H+CH_3CO_2H.$$

Cautious repetition of Varrentrapp's experiment has shown[5] that extensive scission of the chain can with care be largely avoided, and a mixture of isomeric octadecenoic acids thereby obtained. It is clear, therefore, that, given sufficiently rigorous conditions of temperature and alkali concentration, double-bond shift in a monoölefinic substance can be carried out from carbon to carbon atom along a lengthy chain, and this capacity must be regarded as a potentiality in all monoölefins and unconjugated polyenes. It has not been found possible to move the double bond in oleic acid from the original position in more than one direction, *i.e.*, towards the carboxyl group.

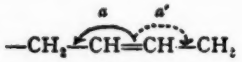
In view of the greatly superior ionizing capacity of methylenic hydrogen in the systems:

$$-CO-CH_2-CO- \quad \text{and} \quad -CH=CH-CH_2-CO-,$$

compared with that in the system $R-CH_2-CO-$, it may be concluded that the double-bond displacements most likely to occur (alternatively) in the system (A) are those indicated by a and a', and these will appear concomitantly with detachment of a proton from the central methylene group (preferentially



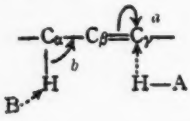
(A)



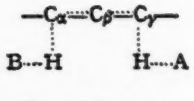
(B)

to detachment of a proton from either of the outer methylene groups). In the case of the system (B), the double-bond shift, under suitably drastic experimental conditions, may be either to left or to right, with corresponding ionization of hydrogen from the adjoining methylene group on the left or on the right.

If we consider the three-carbon system (C) in terms of Ingold's concept of prototropic mechanism, removal of a proton Cα by the base B and comple-

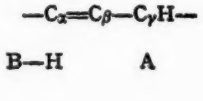


(C)



Transition state.

(D)

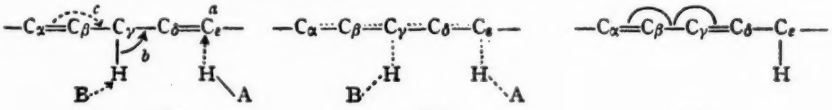


(E)

mentary and concurrent supply of a proton to Cγ by some substance in the system together constitute a process with a definite activation energy (say E). This energy, equal to the difference in energy between the transition state (D) and the initial state C, may be considered to be reduced by a quantity x, due to the polarizations a and b, and representing resonance energy resulting from the electron distribution symbolized by a and b. If the process actually does occur, then the system becomes (E), *i.e.*, the process necessitates a double-bond shift,

which in the absence of an imposed external constraint and with an energy in the system after the change essentially the same as before it(as, *e.g.*, in a purely hydrocarbon system with only saturated carbon atoms beyond the three-carbon system) may be in either direction. But, since in the case of oleic acid, double-bond displacement not only succeeds but apparently proceeds only in one direction (towards the CO_2^- group), it must be concluded both that the required activation energy $E-x$ is actually developed under the conditions of alkali fusion, and that the negative charge on the CO_2^- ion exercises a sufficient, albeit a very feeble, inductive influence through a chain of six saturated carbon atoms (or alternatively through the medium) to determine that a hydrogen atom is detached from C_8 in the system $-\underset{11}{CH_2}-\underset{10}{CH}=\underset{9}{CH}-\overset{\delta+}{\underset{8}{CH_2}}\rightarrow(CH_2)_6\rightarrow CO_2^-$ in preference to one from C_{11}, *i.e.*, to ensure that a transition state involving the three-carbon system C_8-C_{10} rather than one involving the system C_9-C_{11} becomes operative.

Turning to the diene system (F), the activation energy of the isomerization which applies to the simple three-carbon system (*i.e.*, $E-x$) will here be further reduced by a quantity, y, due to incipient conjugation resulting from the polarization c, so the activation energy is $E-(x+y)$; and since a condition of com-



plete conjugation of the double bonds finally ensues, the resonance energy corresponding to this condition reduces the energy of the system (say by Y), so that the degree of conjugation in the transition state will be less than in the final state, *i.e.*, $y<Y$[7]. But it is important to note that the process which gives rise to Y is that which in a less complete manner gives rise to y. The double-bond displacement then in the diene system is likely to be more easily achieved than in the monoölefinic system and, since the same (central) methylene group loses a proton, whichever of the two three-carbon systems comes into play, the occurrence and direction of displacement are likely to be largely unaffected by polar groups terminating the carbon chain. From similar considerations it appears that double-bond displacement in rubber and polyisoprene hydrocarbons is unlikely to occur with an facility under alkali treatment, if at all.

It is of some interest that the polyisoprene hydrocarbon, squalene ($C_{30}H_{50}$), shows a persistent exaltation of the molecular refraction of 1.6 units and the normal-chained unconjugated fish-oil acid, docosahexaenoic acid ($C_{22}H_{32}O_2$; F6), one of 0.8 units[8], provided that each compound is scrupulously freed from its autoxidation products. Rubber also shows the same anomaly. Whether these exaltations are significant and refer to an element of conjugation in the polyene chain analogous to that shown for the diene system in formula (G), which exists in spite of the fact that the double bonds are here separated by two methylene groups, remains to be tested by other methods.

DOUBLE-BOND DISPLACEMENT BY HEAT

The above-mentioned optical anomalies were at first thought to be due to conjugation brought about by progressive heat-isomerization during slow frac-

tional distillation of the high-boiling substances; but this was not the case, since the anomaly appears in specimens which have not been heated above 100°. Prolonged heating of these latter specimens in entire absence of oxygen at temperatures a little below their decomposition points has caused no changes in the absorption spectra which can be attributed to conjugation. Yet at high temperatures (above 270°, or possibly at somewhat lower temperatures in presence of a contact catalyst) olefinic hydrocarbons and esters of vegetable oil acids give polymerized and cyclized products, whose constitutions are such that conjugation can be fairly definitely concluded to have preceded polymerization or cyclization[9]. This isomerization must be attributed to radical dissociation of α-methylenic hydrogen atoms.

VULCANIZATION

The process of vulcanization is usually hastened by the use of organic accelerators, some of which can themselves act as efficient vulcanizers, even when no sulfur is present. The basis of the success of these self-sufficient compounds appears to be their capacity for decomposing thermally to give free radicals, which then act precisely analogously to dibenzoyl peroxide[10] and bring about direct C–C linking of the rubber units at the α-methylenic carbons atoms; tetramethylthiuram disulfide,

$$Me_2N-CS-SS-CS-NMe_2,$$

one of the most efficient of these is a close sulfur-analog of dibenzoyl peroxide, and polyalkylhydrazines, which are prone to decompose thermally to give radicals, have been found to have a vulcanizing effect. Where sulfur alone, or sulfur together with an accelerator, forms the vulcanizing agent, three processes of bridging seem to be possible, *viz.*, (1) direct C–C linking at the α-methylene groups caused by radicals derived from peroxidic chain-starters contained in the rubber, or by radicals derived from the decomposing accelerator, or by radicals derived from the decomposing accelerator, or by atmospheric oxygen:

$$>CH_2 + R^\bullet \longrightarrow >CH^\bullet + RH\,;\ >CH^\bullet + >CH_2 \longrightarrow >CH{-}CH< + H^\bullet,$$

(2) sulfur bridging at the α-methylene group, initiated by chain-starters:

$$>CH_2 + R^\bullet \longrightarrow >CH^\bullet + RH \xrightarrow{S} >CH{-}S^\bullet + RH\,;$$
$$>CH{-}S^\bullet + >CH_2 \longrightarrow >CH{-}S{-}CH<\dagger + H^\bullet,$$

and (3) C–C linking brought about by sulfur functioning purely as a hydrogen acceptor:

$$2>CH_2 + S \longrightarrow >CH{-}CH< + H_2S$$

With regard, however, to the mechanism by which sulfur becomes steadily and extensively incorporated in rubber during the later stages of reaction, with concurrent loss of the unsaturation of the latter, it would be unprofitable without further investigation of sulfur-olefin reactions to attempt to formulate the precise sequence of events. There are, however, two possibilities of double-bond saturation in the vulcanization reaction which do not necessitate recourse to postulation of the direct addition of sulfur in one or other of its known modifications at the double bonds. The first is addition at the double bonds of hydrogen sulfide generated by the attack of sulfur at the methylene groups

(Equation (*c*) above)—an addition which is known to be catalyzed by sulfur, and the second a reaction analogous to that by which a molecule of oxygen becomes attached to an olefin at an α-methylene group:

$$[—CH(OO^{\bullet})—CH{=}CH— \text{ or } —CH(OOH)—CH{=}CH—]$$

and then by secondary reaction attacks and saturates (inter- or intramolecularly) a nearby double bond.

THE PHOTOGELLING OF RUBBER

This phenomenon is one of a group of insolubilization reactions which are of embarrassingly frequent occurrence in connection with the manipulation of rubber and its derivatives, and for which the exact cause usually remains obscure. Solutions of rubber containing such sensitizers as ketones, aldehydes, carbon tetrachloride, chloroform, peroxides, etc., undergo rapid gelling in sunlight, the best sensitizers being those which break down photochemically to give free radicals, and the poorest comparatively stable substances such as pure petroleum fractions and benzene. The very considerable extent to which fragments from the sensitizers or photochemically decomposing solvents enter into the composition of the photogels, leaves little doubt as to the radical nature of the reaction, and there seems to be no difference at all in reaction principle between the type of combined cross-linking and radical addition here encountered and that observed with rubber containing thermally decomposing dibenzoyl peroxide molecules. The increasing toughness of the photogels with increasing degree of reaction (increasing cross-linking) is impressive.

The role of oxygen in the photogelling reactions seems from the observations of Stevens to be a mixed one. As in the case of the substitutional chlorination of olefins, traces of oxygen appear to function catalytically, although in this case the gelling promoted is very slow; larger proportions of oxygen on the contrary hinder oxidation, and serve to cause severe oxidative degradation of the gels.

The above paper and the two preceding ones relate to subjects forming part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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THE LONG SPACING IN RUBBER *

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The x-ray diagrams of some rubbers give a long spacing, which was first reported by Clark and collaborators[1]. According to them, it is found only in gel rubber, where it has the value of 54 A.U., but it is absent in sol rubber[2]. This spacing is oriented in stretched rubber, the x-ray reflections contracting into two spots in the equatorial plane. This means that the long spacings lie in planes at right angles to the fibre axis. As we found it difficult to account for this result and, furthermore, had indications that this long spacing might depend on the nature of the rubber, we examined a number of specimens of different origin and preparation. We used a camera of about 10-inch radius, reducing the air scattering by inserting an evacuated length of wide tube with thin cellophane windows at both ends. The x-ray source in these experiments was the 50 kw. x-ray generator of this laboratory, working with an input of 30 to 40 kw.

TABLE I

Evaporated standard Revertex (about 70% dry rubber content)	36.8
Electrodeposited Revertex, vulcanized (North British inner tube)	37.1
Evaporated latex (38-40% dry rubber content)	41.9
Smoked sheet (I)	45.0
Crepe (I)	46.0
Smoked sheet (II)	46.3
Evaporated vulcanized latex (from 58-60% dry-rubber-content latex)	48.7
Evaporated Centratex (58-60% dry rubber content)	49.5
Evaporated Jatex	49.6
Evaporated creamed latex (58-60% dry rubber content)	49.9
Crepe (II)	none

on a copper target. The specimens were stretched for the examination, and photographs were taken on film strips perpendicular to the fibre axis and beam. The accuracy of an individual measurement comes to ± 1 A.U. in the relevant range.

Table I gives the mean values of the long spacings of some commercial products. The spacings vary over a wide range, but in no case has a spacing of 54 A.U., as given by Clark and collaborators, been found.

The list has been drawn up in order of the values of the long spacings, and it appears that this order reflects the purity of the latex from which the specimen is made. Revertex, it is claimed, contains, in spite of its high rubber concentration, all the substances naturally occurring in latex. Apart from that, the manufacturers add soaps as stabilizing media. The latex with 38 per cent dry rubber content represents a slightly concentrated product which has already lost some of the substances contained in the serum. The preparation of smoked sheet and crepe involves a purification of the raw rubber, and finally, the process leading to the latices with 58-60 per cent dry rubber content reduces the amount

* Presented at a General Discussion on "The Structure and Reactions of Rubber", held by The Faraday Society in London, May 29, 1942. Permission has been generously granted to reprint this paper in RUBBER CHEMISTRY AND TECHNOLOGY.

of impurities even more, as is well known. It should be noted that one of the crepe rubbers did not show a long spacing.

These considerations lead to the assumption that the long spacing is actually due to the natural impurities of the rubber. The protein content does not appear to be responsible for it. Jatex centrifuged to a protein content of 0.1 per cent gives the same spacing as the original Jatex. It is different with the acetone-soluble impurities. Three specimens, *viz.*, inner tube, latex rubber with 38-40 per cent dry rubber content and latex rubber with 58-60 per cent dry rubber content lost the long spacing after thorough extraction in acetone vapor. Similarly, a rubber of particular purity and homogeneity, *viz.*, the "intermediate fraction" of Bloomfield and Farmer[3], gave no indication of a long spacing.

Clark and collaborators raise the question whether the long spacing observed by them is possibly the higher order of an even longer spacing. We have tried to answer this question by examining Revertex, which has the shortest spacing and gives the strongest reflection, in a higher dispersion camera of about 18-inch radius. Spacings up to 95 A.U. should have been observable in this arrangement, but actually only the spacing of 37 A.U. was found.

The nature of the long spacing becomes much clearer when investigating it with respect to higher orientation. These experiments were carried out on a 10-cm. camera, so that the orientation of the rubber could be checked at the same time. Revertex, which, as just mentioned, gives both the shortest and the strongest spacing, was used for this examination.

A stretched strip of such dimensions that the distribution of the crystallites around the fibre axis is at random gives the following results. When the primary x-ray beam strikes the strip at right angles to the fibre axis, the long spacing reflection gives spots in the equatorial plane, no matter what the orientation of plane of the strip. When, on the other hand, the beam is parallel to the fibre axis, a ring is observed. This means that the long spacings are distributed at random in a plane at right angles to the fibre axis.

If the rubber is stretched under such conditions that it crystallizes in a higher orientation, a different result is obtained. The higher orientation was produced by stretching a band and preventing side contraction in its own plane[4]. In this case spots are found only when the beam is parallel to the plane of the band. The long spacing is not observed when the beam is perpendicular to the plane of the band. The orientation of the fibre axis has no influence. This means that the long spacings are oriented at right angles to the plane of the band.

The explanation of this result is drawn from a comparison with an artificial long spacing, as it were. We dissolved some of that crepe which did not give a long spacing and 2 per cent of stearic acid in a common solvent. The long spacing of stearic acid (39.6 A.U.) appears in the x-ray diagram of the rubber obtained after evaporation of the solvent. The interesting point is that this long spacing when observed in stretched rubber exhibits the same orientation effects as those of Revertex. Figures 1 to 3 illustrate this result. The long spacing is strong enough to show a number of the higher orders, which extend into short arcs in the case represented by Figure 3. Revertex gives similar diagrams, with a slightly different long spacing. Apart from that, two faint Debye rings appear, corresponding to the side spacings of stearic acid. Stearic acid normally crystallizes in flakes. The long spacing is approximately perpendicular to the plane of the flakes[5]. If one assumes that stearic acid crystallizes in the rubber in tiny flake-shaped crystals, the orientation effects are completely explained by the mechanical action of the side contraction produced by stretching. The rubber

strip, contracting to about an equal degree parallel and perpendicular to its plane, exerts pressure on the flakes, orienting them parallel to the fibre axis. The rubber of higher orientation contracts only perpendicularly to its own plane, and forces the flakes into the plane. The lengths of the arcs produced by the higher-order reflections in Figure 3, and their angular intensity distributions,

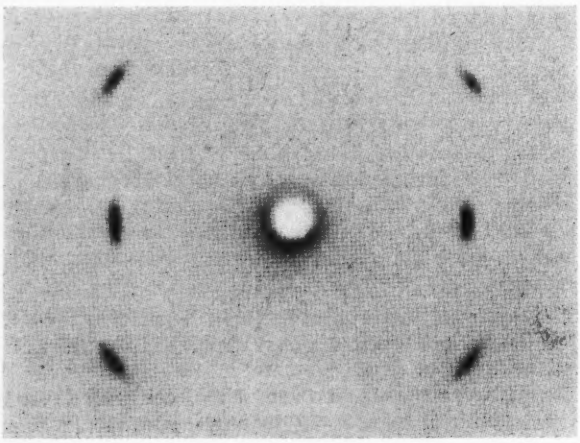

FIG. 1.—Beam perpendicular to plane of specimen.

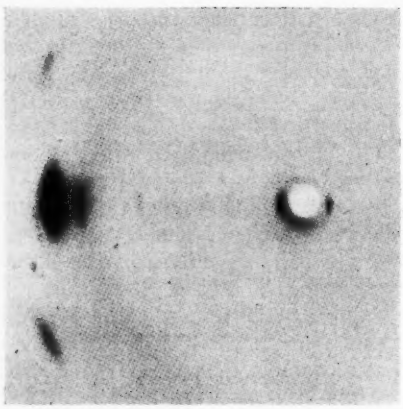

FIG. 2.—Beam parallel to plane of specimen, perpendicular to fibre axis.

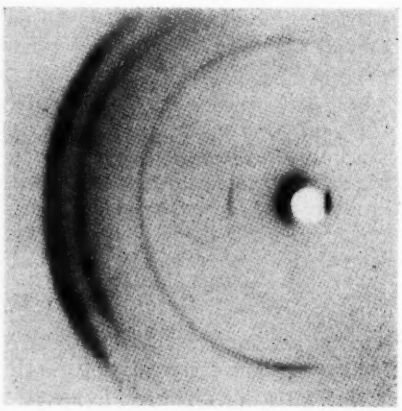

FIG. 3.—Beam parallel to fibre axis.

FIGS. 1 to 3.—Crepe solution rubber with 2 per cent stearic acid stretched to crystallize in higher orientation.

are obviously a measure of the orientation. A comparison with the rubber reflections, which also are arcs, shows that the rate of the higher orientation of the rubber is about the same as that of the stearic acid crystals.

It is a common experience that long-chain compounds, such as some of the acetone-soluble impurities of rubber, crystallize in flakes similar to stearic acid. We conclude from the identical orientation effects that the rubber impurities

crystallize in flat crystals, and so give rise to the observed long spacings. They further accommodate themselves to the altered geometrical dimensions when the rubber is deformed. This is also borne out by the fact that a strong long-spacing reflection is obtained from the surface of an inflated rubber balloon[6]. It is interesting to note that an orientation of suitably shaped crystals can be brought about by embedding them in rubber. It remains to account for the lack of side spacing reflections in the x-ray diagrams. Only a detailed study of the compounds which are responsible for the long spacings can shed light on this point.

We come to the following conclusions. The long spacings found in some rubbers are due to acetone-soluble impurities. They appear to crystallize in flake-shaped crystals, which are oriented when the rubber undergoes deformation.

My thanks are due to the late Sir William Bragg, and to the Managers of the Royal Institution for the facilities granted to me in the Davy Faraday Research Laboratory, and to A. Müller for his great interest in the progress of this work.

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THERMODYNAMIC STUDY OF THE ELASTIC EXTENSION OF RUBBER *

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The kinetic theory of the elasticity of high-molecular substances, propounded by Meyer, von Susich and Valkó[1] and developed statistically by Kuhn[2] and others, has provided a satisfactory basis for the understanding of the essential nature of the elasticity of rubber. The theoretical treatment deals with a highly idealized system, and it is important to see how far the conclusions may be applied quantitatively in the case of real substances. Certain limitations are evident at once. In its simple form the theory is concerned with the elasticity of a single molecule; in a piece of rubber, elasticity can appear only if there are forces between the molecules sufficiently strong to prevent their slipping bodily past one another. This requirement conflicts with the postulate of the statistical theory that intermolecular forces are small, so that the molecular chains are free to take up configurations having the greatest probability or maximum entropy. The bearing of these two opposing conditions on the elastic and plastic behavior of rubber has been discussed elsewhere[3]. A further complicating factor arises from the well-known tendency of rubber to crystallize on stretching, a process which evidently is accompanied by decreases in both internal energy and entropy. How far, in any given case, the observed elastic properties can be satisfactorily accounted for in terms of the simple theory is a matter to be determined by experiment. It is the purpose of this paper to consider the bearing on this problem of the experimental data on the thermal phenomena accompanying the stretching of rubber.

THERMODYNAMIC BASIS

A derivation of the equations relating the entropy S and internal energy U with the tension F and length l of the rubber has been given by Wiegand and Snyder[4]. These equations are:

$$F = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= \left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial F}{\partial T}\right)_l \quad . \quad . \quad . \quad . \quad . \quad (2)$$

They are analogous to the equations for a gaseous system in which pressure P and volume V are replaced by $-F$ and l, respectively[5]. They show that both the increase in internal energy, $(\partial U/\partial l)_T$, and the decrease of entropy, $-(\partial S/\partial l)_T$, on isothermal extension can be calculated from observations of the tension and its temperature variation at constant length. Alternatively, these

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quantities can be obtained by direct measurement of the heat q absorbed during isothermal extension, together with the tension F, for the corresponding entropy change is given by:

$$\left(\frac{\partial S}{\partial l}\right)_T = \frac{1}{T}\left(\frac{\partial q}{\partial l}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the extension is adiabatic, the temperature rise per unit extension, $(\partial T/\partial l)_S$, is given by[6]:

$$\left(\frac{\partial T}{\partial l}\right)_S = \frac{T}{c_l}\left(\frac{\partial F}{\partial T}\right)_l \quad . \quad . \quad . \quad . \quad . \quad (4)$$

c_l being the specific heat at constant length. The temperature rise on adiabatic extension is related to the heat absorbed during isothermal extension by the equation (obtained from 3 and 4):

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{1}{c_l}\left(\frac{\partial q}{\partial l}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (5)$$

EXPERIMENTAL DATA

Data have been obtained by a number of workers both from the stress-temperature relations and by direct thermal measurements; these will now be considered in turn.

1. Stress-Temperature Relations

It would appear to be a simple matter to determine F and $\partial F/\partial T$ at constant length. In practice, many difficulties arise, as a result of which the available data are limited either in accuracy or in the range of extensions covered. These difficulties are due to hysteresis and relaxation phenomena, which interfere with the attainment of well-defined, reversible states.

Meyer and Ferri[7], working up to 350 per cent elongation, obtained reversible stress-temperature curves in the case of a well-vulcanized rubber. After correcting for thermal expansion, they found the relation:

$$F = bT \qquad (b = \text{const.})$$

to hold over a wide range of temperatures. This gives $(\partial U/\partial l)_T = 0$ (Equation 2). Meyer and Ferri's work thus provided the first direct experimental proof of the applicability of the kinetic theory to rubber, at any rate in this region. At very high extensions, however, $(\partial F/\partial T)_l$ was negative. The corresponding large positive value of $(\partial U/\partial l)_T$ indicated that here the elasticity was to be attributed to a different mechanism, which they considered to be the deformation of the valence angles of the stretched molecular chains. In the intermediate regions (350-700 per cent), reversibility was not achieved, owing to hysteresis resulting from crystallization phenomena.

Ornstein, Wouda and Eymers[8] obtained reversible stress-strain curves for a vulcanized rubber in the region 0-250 per cent elongation, but found large hysteresis effects at higher elongation. Table I compares the values of $\left(\frac{F_2 - F_1}{F_1}\right)_l$ with $\frac{T_2 - T_1}{T_1}$; here the calculations are based on their Figure 2. T_1 and T_2 were

294° and 372°, respectively. A correction was applied for the effect of thermal expansion.

It is seen that the force is approximately proportional to the temperature (to an accuracy comparable with the experimental errors). This result is in agreement with that of Meyer and Ferri.

Wiegand and Snyder adopted a rather different method. The tension at a given length l was found in general to depend on the direction from which l was approached but, after performing a series of cycles of extension to $l+\Delta l$ and retraction to l, consistent tensions were finally obtained at both limits of the cycle. The mean of the two corresponding values of tension was then taken to be the true equilibrium value corresponding to an extension midway between the extremes.

This method is open to criticism. If we assume that the tension at a given length and temperature is a function of the amount of crystallization, then the

TABLE I

DEPENDENCE OF FORCE ON TEMPERATURE (AT CONSTANT LENGTH)

(From Ornstein, Wouda and Eymers' Curves)

Elongation (percentage)	$\left(\frac{F_2-F_1}{F_1}\right)_l$	$\frac{T_2-T_1}{T_1}$
50	0.292	0.265
100	0.232	0.265
200	0.221	0.265

TABLE II

INTERNAL ENERGY AND ENTROPY CHANGES ON STRETCHING

(From Wiegand and Snyder's Curves)

Extension (percentage)	F (g. wt.)	$(\partial U/\partial l)_T$ (g. wt.)	$T(\partial S/\partial l)_T$ (g. wt.)
158	70	+ 20	− 50
288	104	+ 24	− 80
376	121	+ 5	−116
462	113	−142	−255
548	131	−240	−371
632	156	−170	−326
718	250	+390	+140

upper end of the elementary cycle, which is approached from a lower state of crystallinity, corresponds to a lower-than-equilibrium amount of crystallization, and hence the observed tension is higher than the equilibrium tension. Similarly, at the lower end of the cycle the observed tension is too low. This is the reason why Wiegand and Snyder's "elements" do not fit into a smooth curve. The taking of a mean value between these points is true only to a first approximation, and cannot be expected to give accurate results when Δl is large, as it was in their experiments.

Nevertheless theirs is the only work of this kind which attempts to cover the whole range of extension, and the data obtained are of considerable interest. The figures given below (Table II) are derived from their curves (Figures 7 and 10). Owing to the absence of information on the cross-section of the specimens employed, it is not possible to convert these figures to calories per gram of rubber.

In region A (0-350 per cent) $(\partial U/\partial l)_T$ was positive but small compared with $-T(\partial S/\partial l)_T$. This means that the entropy of molecular extension was here the

important factor. In region B (350-700 per cent) there was a large decrease both of internal energy and of entropy. It is in this region of extension that crystallization becomes important, and it is evident that we are here dealing with the heat and entropy of crystallization. In region C (700 per cent upwards) there was a large increase of internal energy, due probably to the predominating effect of distortion of the valency angles. The steep rise in the stress-strain curve is another aspect of the same effect.

Hauk and Neumann's experiments.—Meyer has pointed out[9] that if the relation between tension at constant length and temperature is linear, *i.e.*, if:

$$F = aT + b$$

then by comparison with Equation (1):

$$-(\partial S/\partial l)_T = a \quad \text{and} \quad (\partial U/\partial l)_T = b$$

The slope and intercept of the tension/temperature plot thus gives the changes in entropy and in internal energy directly. Such a linear relation between tension and temperature was found by Hauk and Neumann[10] over the range 20° to

TABLE III

INTERNAL ENERGY, ENTROPY, AND HEAT EVOLUTION ON STRETCHING

(Calculated from Hauk and Neumann's Data)

l (percentage)	$(\partial U/\partial l)_T$ (cal. per g. per 100 per cent)	$\int_0^l (\partial U/\partial l)_T dl$ (cal. per g.)	$-\int_0^l (\partial q/\partial l)_T dl$ (cal. per g.)
100	0.04	0.05	0.04
200	0.03	0.09	0.14
300	0.03	0.13	0.29
400	−0.06	0.13	0.50
470	−0.32	0.00	0.82

70° C for a number of differently vulcanized rubbers. Their curves, which were reversible, yield small positive values of $(\partial U/\partial l)_T$ in region A, followed by increasing negative values in region B, in accordance with Wiegand and Snyder. Region C was not reached, the extensions being limited to 470 per cent. No new features are brought out in this work, but the data are sufficient to enable the absolute values of the thermodynamic quantities to be calculated. Table III gives the internal energy increment per cc. of rubber per 100 per cent extension, $(\partial U/\partial l)_T$, the total change in internal energy on stretching to elongation l, $\int_0^l (\partial U/\partial l)_T dl$, and the total heat evolution, $-\int_0^l (\partial q/\partial l)_T dl$, calculated by the author from the data on Hauk and Neumann's sample III*a*, in which the effects of crystallization were most marked.

Houwink's criticism.—Houwink[11] has argued that the small value of $(\partial U/\partial l)_T$ in region A does not prove that internal energy changes are negligibly small, but that there may be an approximate balance between large changes of opposite sign. This view is based on Mack's model of the rubber molecule, which postulates large attractive forces in the molecule tending to restore it to a tightly wound form. The internal energy taken up by the extension is considered by Houwink to be balanced by the energy liberated by crystallization or aggregation. For this argument to apply it is necessary to assume that considerable crystalli-

zation (or aggregation) takes place below 350 per cent extension, and Houwink suggests that the crystallites formed may be too small to form an x-ray fibre pattern. More recent data on crystallization obtained by x-ray[12] and optical[13] investigations give no support to this view.

General conclusion.—The conclusions drawn by Meyer and Ferri, and supported and extended by the other work discussed above, must therefore be regarded as sound. It is evident that the force of retraction is due primarily to the reduction of entropy on extension, as postulated by the kinetic theory. This seems to be true up to about 700 per cent extension, though the simple effects may be masked by internal energy changes due to progressive crystallization. Beyond 700 per cent extension, positive internal energy changes predominate and the negative entropy effect tends to disappear. In this region, therefore, the kinetic theory no longer describes the elastic processes, which are probably similar to those occurring in a typical crystal.

2. Thermal Measurements

Joule's original measurements[14] on the temperature changes accompanying the extension indicated a very slight heat absorption at low elongations, followed by an increasing evolution of heat at higher elongations. The heat evolution was attributed by Hock[15] as early as 1924 to a change of state analogous to crystallization, a view which was supported by his experiments on the fibrosity of stretched rubber, and which received a striking confirmation in Katz's subsequent x-ray investigations[16].

A number of workers have since attempted to measure the heat transfers accompanying extension. Hock and Bostroem[17], by calorimetric measurements of the heat of swelling of stretched and unstretched raw rubber, obtained by difference the heat of retraction. This varied in a roughly linear manner from 0 at 100 per cent to 6.8 calories per gram at 820 per cent elongation. These quantities are very large compared with the thermal equivalents of the work done on the rubber during the extension. Ornstein, Wouda and Eymers[8] measured the temperature rise on extending vulcanized rubber up to 220 per cent extension. The maximum observed ΔT was 1.0 C. No cooling was obtained at low extensions. Their work is of particular interest because they were able to compare the directly measured ΔT value with that calculated from the stress-strain relations at different temperatures. The equation used was equivalent to Equation (4) above, but c_1 was measured directly at various elongations. The agreement between the calculated and observed values of ΔT was reasonably good[18]. Williams[19] measured the temperature rise due to rapid extension of vulcanized rubber. The maximum temperature rise of 4.2° C at 600 per cent extension was equivalent to a heat evolution on isothermal extension of 2.0 calories per gram (Equation 5), which exceeded the work of extension only slightly, indicating a relatively small internal energy change. No cooling was observed at low extensions. Gleichentheil and Neumann[20], who measured the heat evolution in vulcanized rubber calorimetrically, found a very rapid increase between 500 and 700 per cent extension, the maximum (at 800 per cent) being 3.8 calories per gram. Though the corresponding work of extension was not recorded, this large increase was probably due to crystallization. The figure of 3.8 calories per gram corresponds to a temperature rise, under adiabatic conditions, of about 9.5° C, which is higher than any obtained by direct measurement. Quantitative agreement between differently vulcanized rubbers is not to be expected, but reference may be made to Vogt's comment[21] on the fact that the highest temperature rise re-

corded directly is not more than one-third of the temperature rise which he estimates from crude sensory impressions to occur, *i.e.*, 13° C. The author[22] has obtained a rise of 12° C (measured by means of a thermocouple) on stretching vulcanized rubber to 550 per cent elongation. This seems to confirm Vogt's estimate and, since it is equivalent to a heat evolution on isothermal extension of about 4.8 calories per gram, it is not so far removed from Hock and Bostroem's data for raw rubber.

Summing up, the thermal data appear to be neither sufficiently accurate nor sufficiently extensive to give more than a qualitative confirmation of the conclusions drawn from the study of stress-temperature relations. It would be highly desirable to have data obtained by both these methods on the same specimen of rubber over a wide range of extension, together with an independent measurement of the accompanying changes in crystallization. A more exact basis for estimating departures from the simple kinetic theory of elasticity would thus be provided.

SUMMARY

It is shown that the internal energy and entropy changes which take place when rubber is stretched may be determined either by a study of the variation of tension with temperature or by measurement of the heat evolved. The results obtained by a number of authors using both methods are considered. Although quantitative accuracy is not found, the evidence substantiates the kinetic-statistic explanation of rubber elasticity. Crystallization, though giving rise to important thermal effects, is not essentially connected with the phenomenon of elasticity.

This study forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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AN ELASTIC THEORY FOR RUBBER *

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The elastic properties of vulcanized rubber present a difficult problem to generalize, mainly because of the large number of compounds in common use. There are good reasons for many kinds and grades, and a characteristic common to all is large elastic strain. Even in the best grades of rubber these strains are not perfectly elastic, but this is also true of almost all other materials, including spring steels.

An elastic strain theory will be derived for a specific group of rubber compounds, namely, spring stocks. These are dense, strong rubbers, highly elastic

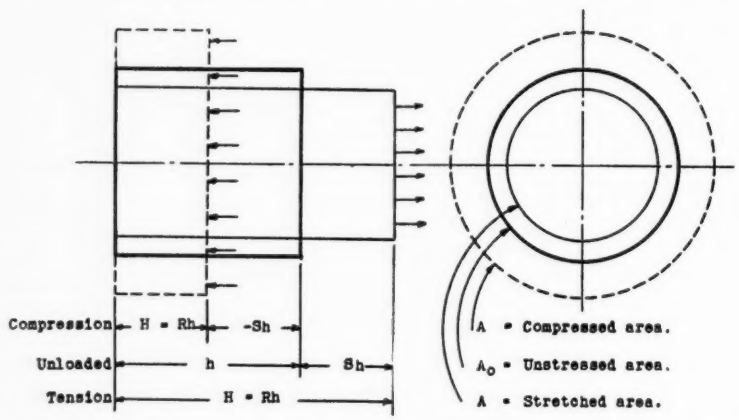

FIG. 1.—Shape alterations of a rubber cylinder resulting from pure tension and compression stresses.

within the working stress range, and capable of supporting loads under continuous vibration and shocks. To be of real value, the strain law should closely predict strain for the range of working stress, or more generally for the elastic range, and should indicate the trend at very high stresses where inelasticity becomes more prominent.

Figure 1 shows a cylindrical element of rubber having an area A_0 and length h when unstressed. If a uniform stress is imposed perpendicular to the end area, the length changes to H and the area to A. These symbols apply whether the stress is tension or compression. The usual definition of strain, *i.e.*, change in length due to stress divided by the unstressed length, is comprehensive and descriptive for the large strains in rubber.

Strain $$S=(H-h)/h. \quad (1)$$

Strain Ratio $$R=H/h=(S+1). \quad (2)$$

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Denote the unit stress by p and modulus of elasticity by E for both tension and compression. By assuming that Hooke's law of elasticity is applicable to rubber, two equations are obtained:

Stress $$p=ES. \tag{3}$$

Load $$P=EA_0S. \tag{4}$$

Equations (3) and (4) are quite accurate for metals, and hold good up to the elastic limit, but such strains are very small, approximating ($S=.005$) for spring steel, and within such limits there is no perceptable change in the area A_0. It is easy to show by tests that these equations predict small strains in rubber and equally easy to show that they fail to indicate large strains accurately. The curves in Figure 2 and Figure 3 were plotted from an actual tension test on one compound, and are typical of other spring stocks, as will be seen later. Since the tests depart widely from the constant slope modulus lines of linear equations (3) and (4), it is evident that Hooke's law is valid only for very small strains in rubber, say up to $S=0.25$, and altogether inadequate for high values.

A first consideration in the revision of Hooke's law of elasticity is the high bulk modulus of rubber. Compounds classed as spring stocks[1] are very dense or solid. Tests show that the bulk modulus[2] varies from $K=300{,}000$ lbs. per sq. in. for soft stocks to $K=400{,}000$ for the hard grades. These are large values compared to the direct modulus $E=150$-400 lbs. per sq. in. for the same range of hardness. Hence, no appreciable error is introduced by assuming the volume to remain constant for the full range of elastic strain. This assumption leads to the equation:

Volume $$V=A_0h=AH=ARh. \tag{5}$$

Equations (3) and (4) are linear, because of the assumption that E is constant, and this is quite accurate for metals. To formulate a large elastic strain for rubber, E might be assumed to be a variable function of stress or strain. This course is not taken due to the departure from the common idea of modulus being a fixed entity for any substance. To adopt a constant direct modulus for rubber requires that it be restricted to some definite load status. A specific definition for E is the slope of the stress-strain curve for zero strain or load. Thus, it is associated equally with tension and compression, and conforms to the definition for metals, where strain is small or nearly zero. Hence:

Modulus of Elasticity

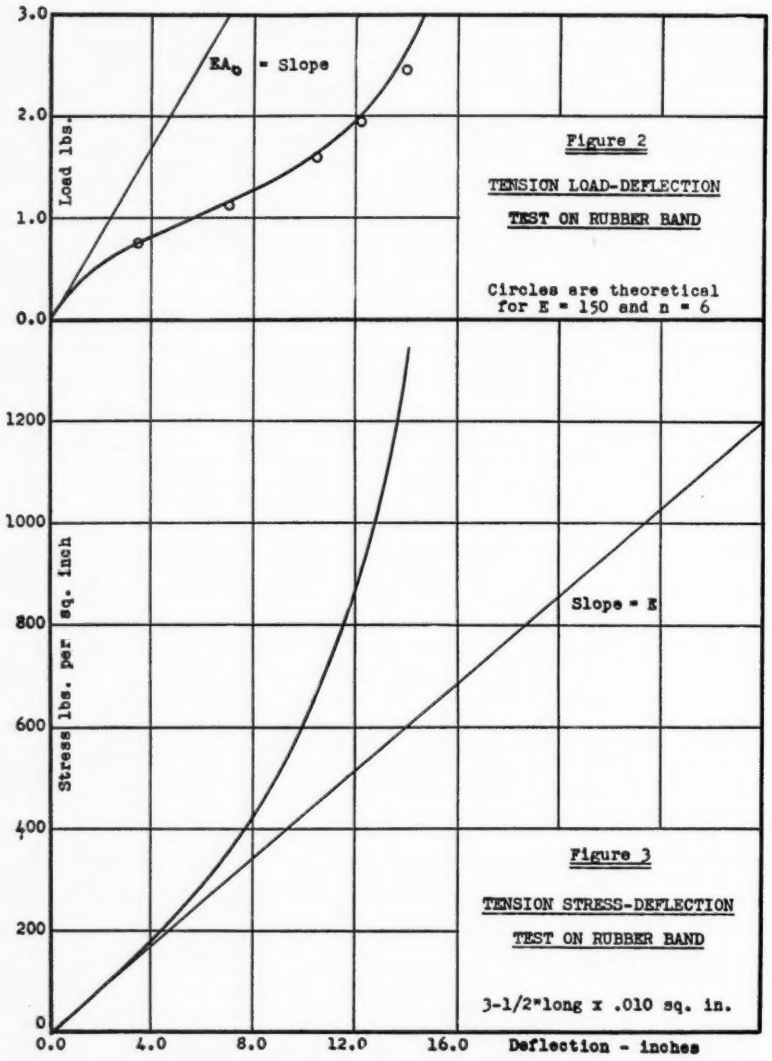
$$E=\frac{dp}{dS}, \qquad \text{where} \qquad S=0. \tag{6}$$

With E defined as a constant, it is necessary to modify Equation (3) to yield a stress-strain graph similar in shape to the test plotted in Figure 3. This might be done by substituting the unknown function $F(S)$ for S, where $F(S)$ is to be derived by a consideration of the physical action of the rubber when subjected to large strains. By the use of $F(S)$, constant volume principle (5), and modulus of elasticity (6), Equations (3) and (4) can be rewritten in the following form, which is applicable to rubber:

$$p=EF(S), \tag{7}$$

$$P=EA_0\frac{F(S)}{R}. \tag{8}$$

Now if all grades of spring rubbers presented similar stress-strain graphs in relation to the E lines, $F(S)$ might be derived empirically. However, as will be shown later, all grades do not follow the same $F(S)$ function, since the cures are not asymptotic to the same strain ordinate. Determining a strain function



empirically for each grade would suggest a difference in the strain behavior of each. It is reasonable to expect similar materials to follow the same basic strain law, in which case the law must contain constants which depend on differences in the various grades.

It is helpful to consider vulcanized rubber made up of very small unit cells sensibly equal in composition. Each cell contains hydrocarbon atoms, some of

which are combined with the sulfur present, also an average proportion of the fillers. These cells are apparently quite rigid, and resist shape distortion from stress, since the x-ray[3] shows stretched rubber to be made up of crystalline units arranged in a fiber pattern, and, when the stress is relieved, the crystalline units are still present but orientated at random. Hence, it appears that the shape alteration of the mass under large strains calls for a redisposition of the unit cells and not a shape change in the cells geometrically similar to the entire mass.

For the purpose of illustrating strain by cell motion, a tensile force is imposed on the axis of a cylindrical element, Figure 4*a*, consisting of a large number of cells. Along the center is a continuous line of cells. Surrounding the core is a tubular volume also filled with cells. All cells are shown spherical for convenience, and no attempt will be made to postulate their real shape. While it is probable that the cells are disposed at random originally, this regular pattern is assumed as an average for further analysis.

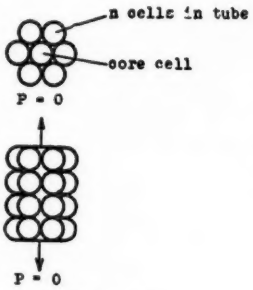


FIG. 4*a*.—Typical cell arrangement in unstressed rubber.

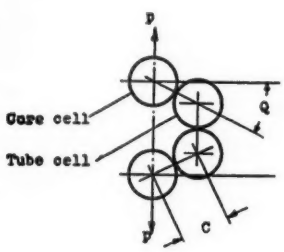


FIG. 4*b*.—Cell movement due to tensile stress.

The entire cross-sectional area of the rubber mass, Figure 1, consists of cylindrical groups of cells like Figure 4*a*, the lengths extending through the mass for a distance h when unstressed. If all these cylindrical groups are stretched by an axial load and the cells maintain their shape, then elongation without rupture calls for drawing the tube cells into the core line, filling up the space which would otherwise occur between the original core cells due to elongation.

Assuming that all cells of like size and shape results in the ideal pattern shown in Figure 4*a*, with six tube cells for each one in the core, one is led directly to the limit of 600 per cent elongation for possible elastic action if the cell distribution is the perfect arrangement shown. If rupture does not occur at 600 per cent stretch, then the cylindrical groups must start robbing from the adjacent elements, which obviously involves inelasticity, since there would be no identication remaining as to the source of the various cells and their complete return prevented when unloaded. If the cell arrangement is not perfectly regular like Figure 4*a*, it is possible that adjacent cylindrical elements may both claim certain cells, leading to inelasticity below 600 per cent elongation.

It can easily be shown that five tube cells for one core cell, all the same size and spherical in shape, is a possible arrangement, provided the two types are staggered along the axis. Allowing some oddities in shape, eight tubes to one core cell appears to be the maximum ratio, since the tube area is eight times the core area.

Now, let us generalize the cell structure, letting n equal the ratio of tube to core cells. Then, the greatest perfectly elastic elongation will be limited to $100n$ per cent. If the unstressed cylinder, Figure 4*a*, has an area A_0 and is loaded by a tensile force P, then by Equation (5) the unit tensile stress is:

$$p=\frac{PR}{A_0}. \tag{9}$$

Figure 4*b* shows the cells spaced by C and rotated through an angle Q by the tensile strain. The strain moment will be:

$$M_s=pC\cos Q. \tag{10}$$

Denoting the resistance to cell rotation by the elastic constant E, and noting that rotation is proportional to S, the moment of resistance to rotation is:

$$M_r=CES \tag{11}$$

also

$$Q=\frac{\pi S}{2n} \tag{12}$$

Equating (10), (11) and (12) gives:

$$p=ES\sec\frac{\pi S}{2n} \qquad \text{(Tension)} \tag{13}$$

by (9)

$$P=\frac{A_0ES}{R}\sec\frac{\pi S}{2n} \qquad \text{(Tension)} \tag{14}$$

Hence

$$F(S)=S\sec\frac{\pi S}{2n} \qquad \text{(Tension)} \tag{15}$$

Transposing (13) and (14) to nondimensional forms:

$$\frac{p}{E}=F(S) \qquad \text{(Tension)} \tag{16}$$

$$\frac{P}{EA_0}=\frac{F(S)}{R} \qquad \text{(Tension)} \tag{17}$$

A compression stress-strain equation can easily be derived directly from the tension Equation (13) by simple reasoning. It is evident that a tension strain ratio R denotes the reverse physical process to a compression strain ratio R' if $(RR'=1)$. For example, by stretching a length h the new length is (Rh), and starting with an unstressed length (Rh) and compressing it by a ratio R', it is shortened to h.

For tension, the cells pulled into the core per unit length is:

$$(Rh-h)/h=(R-1) \qquad \text{Corresponding to stress } p,$$

and compression extrudes cells from the core per unit length by:

$$(Rh-h)/Rh=(R-1)/R \qquad \text{Corresponding to stress } p'.$$

Since the unit stress is proportional to unit cell movement:

$$p'=-pR' \qquad (\text{for } RR'=1). \tag{18}$$

Or a compression strain ratio R' sets up a compression stress equal to R' times the tensile stress from a tensile strain ratio R. Combination of (13) and (18) yields:

$$p' = E(R'-1)\sec\frac{\pi(R'-1)}{2nR'}. \tag{19}$$

Since R is eliminated from (19), the condition ($RR'=1$) no longer applies, and the primes can be dropped, giving the compression equations which follow:

$$p = ES\sec\frac{\pi S}{2nR} \qquad \text{(Compression)} \tag{20}$$

by (9)
$$P = \frac{A_0 ES}{R}\sec\frac{\pi S}{2nR} \qquad \text{(Compression)} \tag{21}$$

and
$$F'(S) = S\sec\frac{\pi S}{2nR} \qquad \text{(Compression)} \tag{22}$$

Transposing (20) and (21) to nondimensional form:

$$\frac{p}{E} = F'(S) \qquad \text{(Compression)} \tag{23}$$

$$\frac{P}{EA_0} = \frac{F'(S)}{R} \qquad \text{(Compression)} \tag{24}$$

It is to be noted that the elastic Equations (13) and (14) for tension differ slightly in form from the compression Equations (20) and(21), this being the result of the strain definition selected. By comparing the nondimensional forms (16) and (17) for tension and (23) and (24) for compression with the original Equations (7) and (8), it is seen that they are alike in form. Since the strain functions $F(S)$ are all secant functions, it is clear that all these strain equations resolve to Hooke's law given by (3) and (4) for infinitesimal strains. This indicates Hooke's law to be a special case of this more general law for large elastic strains.

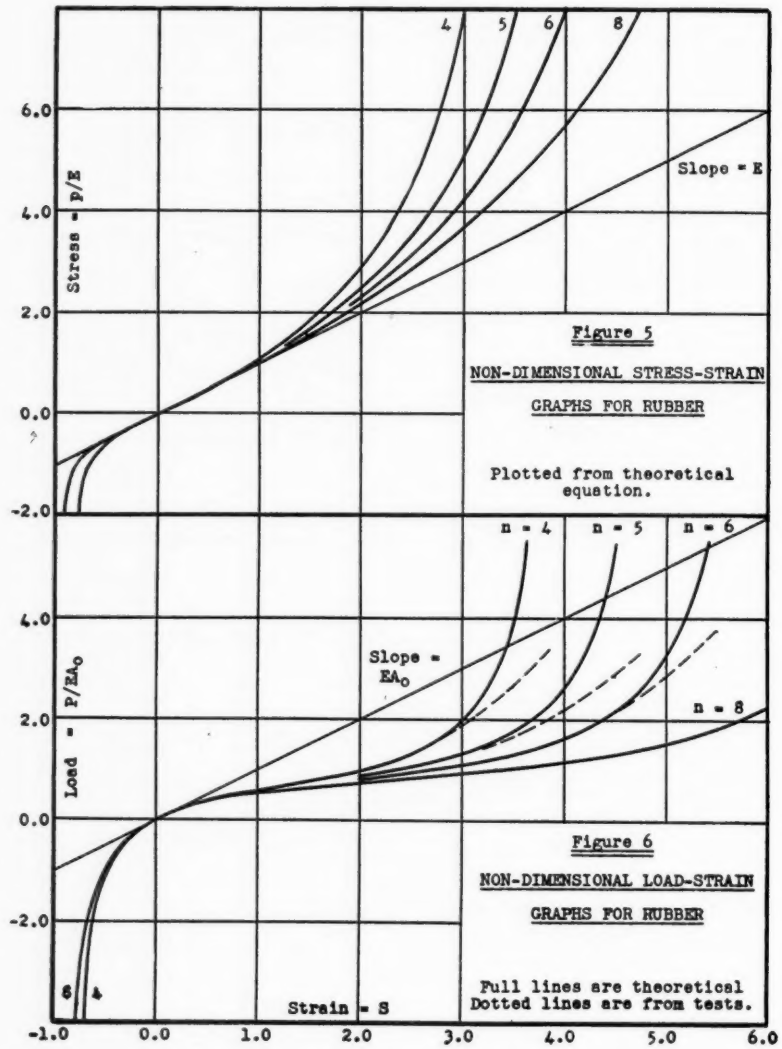
A number of tests will now be cited to support these theoretical elastic strain laws. Figure 2 shows a graph of a tension test made by the author on a band of rubber. For this grade $E=150$ and $n=6$, and the circles represent values computed by Equation (14). The tension strain is accurately predicted up to 400 per cent elongation.

The strain law was further verified by a series of standard tension tests[4] made on commercial spring stocks. Data given below describe three of the grades tested.

Durometer hardness	Direct modulus E	Structure n	Test agreement (Percentage)	Elongation at rupture (Percentage)
29	165	6	450	800
40	225	5	350	700
61	420	4	300	550

Nondimensional strain Equations (16), (17), (23) and (24) are plotted in Figures 5 and 6, using four different n values. The tests of the three rubbers

given in the table above follow these curves accurately up to very high strain values, and the dotted lines branching off from the theoretical curves show where deviation begins. The theoretical curves denote perfect elasticity up to rupture and any departure from elasticity give more strain than is predicted. It is important to note that the test deviations show the proper trend.



The tension and compression tests made by Henchy[5] were compared with this theory for the compound having $E=210$ and $n=5$. All test values agree very satisfactorily over the entire tension and compression range. This agreement is of real importance, since it supports the idea that E applies equally to both tension and compression strains. Tension strain tests are relatively easy to

perform, using a band or the standard tension specimen. Much more difficulty is encountered in compression, the cylinder, Figure 1, must be short relative to the diameter for stability, and the ends must be well lubricated to permit end area expansion with negligible friction. Tests described by Henchy[6] and Kimmich[6] show how pure compression stresses can be accomplished by employing suitable lubricants on the loading faces.

Returning again to the cylindrical cell group shown in Figure 4*a*, a pertinent question is: What determines the identity of the tube and core cells? Their function or identity may depend entirely on chance or be controlled by variations in size, shape or adhesive forces between them. Probably under low strains, lines of core cells are selected at random where the most direct alignment occurs, but when the strain becomes large, core cells are forced to operate at uniformly spaced locations, so the action of cell motion is equalized throughout the volume. Test behavior makes it evident that cell function is not established immediately. The first few test runs show considerable variations, and as many as ten cycles or more must be performed on a new specimen before the results will repeat[7]. This was also pointed out by Kimmich[6] in connection with compression tests.

Aside from immediate uses, such as predicting strain for a specific condition of loading, this elastic strain theory may be of some value to the rubber chemist in the study of fillers and compounds. Possibly it will serve to further emphasize the importance of particle size and shape, as well as the value of uniformity for materials used as fillers. Evidently, the percentage and kind of fillers and other compounding materials influence or establish the structural constant n, since its value changes for different grades. The author was unable to find any commercial compounds corresponding to $(n=8)$; this may be an interesting structure for the chemist to produce. Experiments with fillers and their effect on the structural constant may support or add to the basic theory; or may suggest another mechanical picture of strain which will prove to be more general or useful. If this work constributes in any way to the development of better compounds or their more efficient use, its purpose will be accomplished.

REFERENCES

[1] Cellular or sponge rubbers are excluded. Spring stocks are vulcanized under high pressure, and have specific gravities which are approximately 1.
[2] Bulk modulus values are the results of tests made by the United States Rubber Co.
[3] McNicholas, "x-Ray Analysis of Rubber", Natl. Bur. of Standards.
[4] These tension tests were made by the United States Rubber Co. expressly for the purpose of checking this theory. The author is grateful for this important contribution.
[5] Henchy, "The Elastic Behavior of Vulcanized Rubber". Presented at the meeting of the American Society of Mechanical Engineers, New Haven, Conn., June 22-25, 1932.
[6] Kimmich, "Rubber in Compression". Presented at the meeting of the American Society for Testing Materials, Committee D-11 on Rubber Products, Atlantic City, N. J., June 28, 1940.
[7] The tension-strain tests made by the United States Rubber Co. to check the strain theory brought out this fact.

RUBBER, POLYISOPRENES, AND ALLIED COMPOUNDS

I. THE SYNTHESIS OF LOW-MOLECULAR POLYISOPRENES OF THE RUBBER AND THE SQUALENE TYPE *

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For various purposes in connection with the investigation of rubber, it has been desired to obtain low-molecular, open-chain polyisoprenes in which a uniform head-to-tail arrangement of the isoprene units is strictly maintained. A dimeric rubber in the form of dihydromyrcene:

$$H \cdot (CH_2 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CH_2) \cdot H,$$

is obtainable by reduction of the myrcene hydrocarbon present in Bay oil (*Pimenta acris*), and a hexameric polyisoprene is available in the form of squalene, a well-known component of certain fish-liver oils; but in the latter case the hydrocarbon is not of the rubber type, since the head-to-tail arrangement of C_5-units extends only from each end of the molecule to the middle. No other low-molecular, open-chain polyisoprenes, save one which is discussed below, are known, and there is no general method of passing with structural certainty the polyisoprene series.

The possibility of obtaining a useful selection of relatively low-molecular, straight-chain polyisoprenes from isoprene itself by direct polymerization has been examined concurrently with this work, but the triple requirement of rigid maintenance of the head-to-tail arrangement of units, the exclusion of all chain-branching arising from the 1,2-additive tendency of the diene molecules, and the fairly precise regulation of the chain-length, is a severe handicap to success. The obvious synthetic alternative to the polymeric method, amounting to the building of the chain unit by unit by formal organic methods, could not be other than laborious and expensive, and hence it seemed useful before embarking on it to explore the possibility of applying a third procedure, based on the Wurtz and the Grignard reaction.

Bifunctional Grignard reactions have been known in the saturated series for many years. Von Braun and Sobecki[1] described C_8- and C_{12}-hydrocarbons obtained by such means from 1,4-dibromobutane, and Carothers and his coworkers[2] have since described numerous such reactions, and have closely studied the conditions necessary for promoting the polymolecular type of reaction. Attempts, however, to employ an unsaturated dihalide have led so invariably and so completely to monomeric butadiene by all feasible methods of carrying out the Wurtz and the Grignard reaction that further attempts in this direction have been abandoned.

Rubber type of hydrocarbon.—The most promising approach to unit-by-unit synthesis of straight-chain polyisoprenes of the rubber type seemed to be that afforded by Ruzicka's elegant procedure for building up polyterpene alcohols. From geraniol, he passed by the successive action of phosphorus trichloride,

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acetoacetic ester, acetylene, and nascent hydrogen to a tertiary triisoprene alcohol, nerolidol, and thence with phosphorus tribromide to the bromide of its anionotropic (primary alcoholic) counterpart, farnesyl bromide:

$$\underset{\text{Geraniol}}{\text{Ger.}\cdot\text{OH}}\longrightarrow\text{Ger.}\cdot\text{Cl}\longrightarrow\underset{\text{Geranylacetone}}{\text{Ger.}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3}\longrightarrow$$

$$\underset{\text{Dehydronerolidol}}{\text{Ger.}\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{C:CH}}\longrightarrow\underset{\text{Nerolidol}}{\text{Ger.}\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{CH:CH}_2}\longrightarrow$$

$$\underset{\text{Farnesyl bromide}}{\text{Ger.}\cdot\text{CH}_2\cdot\text{CMe:CH}\cdot\text{CH}_2\text{Br}}$$

$$[\text{Ger.}=\text{CH}_3\cdot\text{CMe:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe:CH}\cdot\text{CH}_2\text{·}.]$$

Further, while the present work was in progress, he has, by the same method, synthesized the tetraisoprene alcohol, geranylgeraniol, $C_{20}H_{33}\cdot OH$, from its naturally occurring triisoprene analogue, farnesol. Thus it has been demonstrated that it is possible to pass from the C_{10}- to the C_{15}-, and thence to the C_{20}-polyisoprene skeleton in the case of alcohols; and further application of the method appears to be limited only by the necessity for using increasingly large quantities of starting material as the series is ascended.

If a ketone of Ruzicka's series, *e.g.*, geranylacetone or farnesylacetone, were to be submitted to the action of a Grignard reagent, a tertiary alcohol might be expected to result, which by dehydration ought to lead to one or more of three hydrocarbons. One of these hydrocarbons should have the correct structure for a member of the straight-chain hydrogen-stabilized (*i.e.*, dihydro) polyisoprene series. We have found that geranylacetone yields smoothly with ethylmagnesium bromide a tertiary alcohol:

$$\text{Ger.}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3\longrightarrow\text{Ger.}\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{CH}_2\cdot\text{CH}_3\xrightarrow{-\text{H}_2\text{O}}$$

$$\text{Ger.}\cdot\text{CH}_2\cdot\text{CMe:CH}\cdot\text{CH}_3\text{ or Ger.}\cdot\text{CH:CMe}\cdot\text{CH}_2\cdot\text{CH}_3$$

$$\text{or Ger.}\cdot\text{CH}_2\cdot\text{CEt:CH}_2$$

dihydronerolidol, which by dehydration with potassium bisulfate yields a triolefinic hydrocarbon, $C_{15}H_{26}$. On ozonolysis, this hydrocarbon gives acetaldehyde and acetic acid in fairly good yield, but no detectable trace of formaldehyde, formic acid, or methylethyl ketone. Furthermore it gives, with dry hydrogen chloride, a 93 per cent yield of a homogeneous trihydrochloride. Now, although all the three isomeric hydrocarbons would be likely to yield in large measure, and probably completely, the same form of the trihydrochloride, yet the ozonolysis result points plainly to the fact that the dehydration product of dihydronerolidol is a pure, or at any rate a substantially homogeneous, *dihydrofarnesene,* $\text{H}\cdot[\text{CH}_2\cdot\text{CMe:CH}\cdot\text{CH}_2]_3\cdot\text{H}$, which represents the (hydrogen-stabilized) triisoprene member of the rubber series; also there seems little doubt that application of the same procedure to geranylgeraniol will yield the corresponding tetraisoprene, $\text{H}\cdot[\text{CH}_2\cdot\text{CMe:CH}\cdot\text{CH}_2]_4\cdot\text{H}$, a result which it is hoped to be able to report later.

Soon after the experiments above had been completed, however, it was found that Jones and Haenke[3], in examining essential oils derived from Queensland flora, had isolated a nerolidol fraction, from which in the course of purification by conversion into the sodium salt they had obtained, as byproduct, a hydrocarbon, $C_{15}H_{26}$, having $d^{5.5°}$ 0.8335, $n_D^{20°}$ 1.4700. This hydrocarbon they concluded to be dihydrofarnesene, since linalool under similar treatment gave dihydromyrcene, and they characterized it by forming a solid hexabromide, m. p. 131°. To confirm the constitution assigned, they prepared for comparison a

reputed dihydrofarnesene by reduction with sodium and alcohol of farnesene derived by dehydration of nerolidol. This hydrocarbon also gave the hexabromide, m. p. 131°.

This property of giving, among the various stereoisomeric forms likely to arise from an unconjugated triisoprene, a solid hexabromide, and also the values assigned to the density and refractive index, distinguish the hydrocarbon from that described above, which had $d_{4°}^{20°}$ 0.8202, $n_D^{20°}$ 1.4712, and did not give a solid hexabromide.

We had realized at the outset that farnesene derived by dehydration of farnesol was unlikely ever to be entirely free from its cyclic triene isomeride, bisabolene, since it cyclizes so easily with acid reagents, among which must be included the potassium bisulfate probably employed by Jones and Haenke[3]. Kerschbaum[4] had dehydrated farnesol by heating it with potassium bisulfate, and obtained a hydrocarbon which Ruzicka[5] subsequently demonstrated to be, not farnesene, but bisabolene. Ruzicka, however, obtained a product with better physical constants ($d_{4°}^{18°}$ 0.8385; $n_D^{18°}$ 1.4965), which he concluded to be farnesene, by distilling off the hydrocarbon from the bisulphate as it was formed; he suggested that farnesene must be

$$C_{10}H_{17} \cdot CH{:}CMe \cdot CH{:}CH_2, \text{ or } C_{10}H_{17} \cdot CH_2 \cdot C(:CH_2) \cdot CH{:}CH_2,$$

or a mixture of both. Later, he synthesized bisabolol[6]. Farnesene having either of the (conjugated) structures suggested by Ruzicka should, of course, give the desired dihydrofarnesene on reduction.

Whether farnesene can be obtained entirely free from bisabolene when postassium bisulfate is used as dehydrating agent does not appear from Ruzicka's observations. We have dehydrated farnesol with this reagent, distilling off the hydrocarbon as it was formed, and so obtained a product having rather a higher density ($d_{4°}^{19.5°}$ 0.8469; $n_D^{19°}$ 1.4945), and probably therefore a rather greater bisabolene content than Ruzicka's. Determination of the unsaturation of this hydrocarbon by hydrogenation gave a value, probably somewhat low through incompleteness of reaction, of $|\overline{\overline{\underset{3.5}{}}}$ per $C_{15}H_{24}$, indicating the presence therein of at least 50 per cent of farnesene; heating with formic acid (Ruzicka's method) caused complete conversion into bisabolene, as shown by the purity of the derived bisabolene trihydrochloride. Reduction of the hydrocarbon with sodium and alcohol gave a dihydrofarnesene having three double bonds (Found, by hydrogenation: $|\overline{\overline{\underset{2.85}{}}}$) and physical constants somewhat higher than those of our hydrocarbon from dihydronerolidol, doubtless due to the substantial proportion of bisabolene present; but the physical constants of this reduction product agreed closely with those of Jones and Haenke's material. Conversion of this dihydrofarnesene into the hydrochloride gave a solid product which was easily separated into two trihydrochlorides, one of bisabolene and one identical with the trihydrochloride of our dihydrofarnesene from dihydronerolidol. Nevertheless, we have not yet isolated from the bromide of this dihydrofarnesene any crystalline hexabromide. We see no reason, therefore, to doubt the substantial purity of our dihydrofarnesene described above, or the correctness of the constitution assigned to it.

Squalene type of hydrocarbon.—With farnesyl bromide as starting point, it is only necessary, as Karrer has shown[7] to couple the hydrocarbon radicals of two molecules of halide by a metal such as magnesium to produce a hydrocarbon identical with natural squalene. Starting, however, from the more readily available geraniol, it is necessary to intercalate a centrosymmetrical diisoprene sys-

tem between two geranyl radicals. This might be expected to be capable of accomplishment, so far as the carbon framework is concerned, by combining two molecules of geranylacetone with the Grignard reagent derived from 1:4-dibromobutane:

$$2\text{Ger.}\cdot CH_2\cdot COMe + MgBr\cdot[CH_2]_4\cdot MgBr \longrightarrow \text{Ger.}\cdot CH_2\cdot CMe(OH)\cdot[CH_2]_4\cdot CMe(OH)\cdot CH_2\cdot \text{Ger.}$$
$$(\text{Ger.} = C_{10}H_{17})$$

As regards the Grignard reagent required, von Braun and Sobecki's experiments[1] indicated that the metallo-organic derivatives $MgBr\cdot[CH_2]_4\cdot MgBr$, $MgBr\cdot[CH_2]_8\cdot MgBr$, and $MgBr\cdot[CH_2]_{12}\cdot MgBr$ are all formed side by side when magnesium acts on 1,4-dibromobutane; also Young, Prater, and Winstein[8] have described optimum conditions for the preparation of the normal Grignard compound from the difficultly reactive crotyl bromide. Since the Grignard product from dibromobutane cannot easily be fractionated before use, we tried to suppress as far as possible the formation of polymeric forms of the metallo-organic compound from 1,4-dibromobutane by using the conditions described by Young and his coworkers. This procedure, probably aided by the preferential tendency for the monomeric rather than the polymeric forms of the dimagnesium halide to react with the geranylacetone, has been successful in yielding principally one compound—a glycol of the expected empirical formula, $C_{30}H_{52}(OH)_2$; there was, however, a residue which probably consisted of the analogous C_{34}-glycol derived from $MgBr\cdot[CH_2]_8\cdot MgBr$.

The C_{30}-glycol showed a molecular refraction 1.5 units higher than the calculated figure, which recalls the exactly similar experience of Heilbron with non-conjugated natural squalene[9] and of Farmer and Van den Heuvel[10] with highly unsaturated fish-oil acids. This phenomenon, which is apparently due either to the inaccuracy of the atomic refractivity values (Eisenlohr's) employed in calculating $[R_L]_D$, or to the appearance of conjugation during heating, is being investigated.

By the action of dry hydrogen chloride on the C_{30}-glycol, there was obtained a mixture of three isomeric hexahydrochlorides, which proved to be identical with the three isomerides first obtained by Heilbron from squalene[11]; and since squalene can easily be regenerated from these hydrochlorides by the action of mildly alkaline reagents, this work constitutes a new synthesis of squalene and also suggests a general method for the synthesis of hydrocarbons of the squalene type. Thus, from farnesylacetone a

$$2\text{Far.}\cdot CH_2\cdot COMe + MgBr\cdot[CH_2]_4\cdot MgBr \longrightarrow \text{Far.}\cdot CH_2\cdot CMe(OH)\cdot[CH_2]_4\cdot CMe(OH)\cdot CH_2\cdot \text{Far.}$$
$$[\text{Far.} = C_{15}H_{25}.]$$

C_{40}-glycol would be expected to result, from which by direct dehydration, or via the derived octahydrochlorides, a C_{40}-polyisoprene hydrocarbon of squalene type might be expected to be formed.

It is on record that farnesol gives with dry hydrogen chloride the same product as does its dehydration product farnesene:

$$\underset{\text{Farnesol}}{H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_3\cdot OH} \xrightarrow{HCl} \text{Tetrahydrochloride}$$

$$\xleftarrow{HCl} \underset{\text{Farnesene}}{H\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_2\cdot CH{:}CMe\cdot CH{:}CH_2}$$

The new C_{30}-glycol, as noted above, gives the same mixture of three isomeric hexahydrochlorides as does natural squalene. To this we now add that the dihydronerolidol whose synthesis is described above gives the same trihydrochloride as does its dehydration product dihydrofarnesene. The yield of hydrochloride from the alcohol was quantitative, whereas that from the hydrocarbon at the first attempt was 93 per cent; and it is of considerable interest that the yields of hydrochlorides of polyisoprenes (including rubber with a molecular weight of about 300,000) seem generally to be quantitative, or very nearly so, under suitable conditions of reaction.

EXPERIMENTAL

Geranylacetone.—Commercial geraniol of good quality was purified by conversion into its calcium chloride compound, essentially the procedure of Bertram and Gildemeister[13] being used. The regenerated geraniol, b. p. 117° (13 mm.) with a 55-60 per cent yield was converted into its chloride, with a 60 per cent yield and thence into geranylacetone by the method of Ruzicka[14]. The rectified ketone boiled at 126-128° (10 mm.), with a 70 per cent yield.

Dihydronerolidol.—To an ethereal solution of ethylmagnesium bromide (6.07 g. of magnesium, 27.2 g. of ethyl bromide, 100 cc. of ether) contained in a 1-liter flask fitted with condenser, dropping funnel, and a mercury-sealed stirrer, a solution of 48.5 g. of geranylacetone in 50 cc. of ether was added gradually with good stirring. The reaction product was boiled for 30 minutes, and then decomposed by gradual addition of excess of water, with good stirring. The stirring was continued while sufficient 2 *N* hydrochloric acid was added to dissolve the magnesium hydroxide, after which the crude dihydronerolidol was extracted with ether, the extract washed in turn with sodium bicarbonate solution and water, and then dried over potassium carbonate. Removal of the solvent gave a product which after suitable fractionation boiled at 137-140° (8 mm.), with a 77 per cent yield. The *dihydronerolidol* was a colorless, odorless, not very mobile liquid; $d_{4^\circ}^{20^\circ}$ 0.8693; $n_D^{20^\circ}$ 1.4690; $[R_L]_D$ 71.73 (Calc. for $|\bar{2}$, 72.06) (Found: C, 80.5; H, 12.7; active H, 0.49. $C_{15}H_{28}O$ requires C, 80.35; H, 12:5; active H, 0.45%).

Dihydrofarnesene.—Dihydronerolidol (20 g.) was refluxed over finely powdered potassium bisulfate for 45 minutes at 18 mm. pressure in a 100 cc. flask fitted with capillary bubbler (bath temp. 160°). The condenser was replaced by a still-head and the liquid product distilled off. The distillate (b. p. 130-140° (15 mm.)) was again refluxed at reduced pressure for 25 minutes with 5 g. of fresh potassium bisulphate, and the product distilled off. The distillate was carefully fractionated over sodium in an apparatus based on that described by Schrader and Ritzer[15], but modified to avoid the strong tendency to evaporative distillation experienced with the apparatus when good oil-pump vacua are employed, and provided with alternative sets of collecting cups. The bulk of the product boiled at 129-131° (11 mm.) with a 65 per cent yield, leaving a liquid residue of higher boiling point. The former was a triolefinic hydrocarbon, *dihydrofarnesene* (Found: C, 86.8; H, 12.7. $C_{15}H_{26}$ requires C, 87.3; H, 12.7%); $d_{4^\circ}^{20^\circ}$ 0.8202, $n_D^{20^\circ}$ 1.4712, unsaturation (iodine value $|\overline{\overline{2.99}}$, $|\overline{\overline{2.97}}$, $[R_L]_D$ 70.29 (Calc. for $|\bar{3}$, 70.07).

Dihydrofarnesene trihydrochloride.—(1) *From dihydrofarnesene.* The hydrocarbon (3.25 g.), dissolved in dry ether (25 cc.) and protected against atmospheric moisture, was saturated at 0° during 1 hour with dry hydrogen chloride.

The ether and excess hydrogen chloride were evaporated, leaving a thick, oily residue which soon solidified in a vacuum desiccator. The crystals of crude *trihydrochloride* (93 per cent yield) melted at 44-47°, but reached a constant m. p. of 52° after one recrystallization from methyl alcohol (Found: Cl, 33.75. $C_{15}H_{29}Cl_3$ requires Cl, 33.70%).

(2) *From dihydronerolidol.* Dihydronerolidol (3 g.), dissolved in dry ether. (100 cc.), when saturated with dry hydrogen chloride as above, gave a white solid (4.2 g.; 100 per cent yield) with m. p. 44-47°, which after one crystallization from methyl alcohol melted constantly at 52°. Mixed m. p. with foregoing trihydrochloride, 52°.

Ozonolysis of dihydrofarnesene.—The hydrocarbon (2.9 g.), dissolved in ethyl acetate (20 cc.) and cooled in an ice-salt bath, was ozonized (1.44 g. of ozone per hour) for 90 minutes, after which the solvent was removed under reduced pressure, with gentle warming, and the residue decomposed by warming and finally boiling with water. The issuing gases were passed through a liquid-air trap, and the steam distillate was fractionated under a short column. The products were: (1) acetone, 0.33 g. (estimated by Messenger's method), identified by 2,4-dinitrophenylhydrazone, m. p. 125°; (2) acetone peroxide, m. p. 130°, 50 mg. (total yield of acetone 47 per cent); (3) acetaldehyde, converted with considerable loss into its dimedon derivative, m. p. 139° (yield 10 per cent), and (4) an aqueous residue containing acetic acid. One-half the aqueous residue was neutralized with standard sodium ethoxide solution (3 g. per l.), and the neutral solution heated with *p*-bromophenacyl bromide. The titre and the yield of *p*-bromophenacyl acetate (m. p. 83°, mixed m. p. 84-85°) both corresponded to 0.2 g. of acetic acid. The remainder of the aqueous residue gave, by extraction with ether, a rather viscous liquid which, by reason of its strong iodoform reaction and the formation of a semicarbazone (m. p. 183°, decomp.), was doubtless impure laevulic acid (semicarbazone, m. p. 187°). No formaldehyde could be isolated from, or detected by color tests in, the condensate in the liquid-air trap or the volatile distillate; and likewise no methylethyl ketone could be isolated or detected.

Dehydration of farnesol.—The farnesol, supplied by C. Naef and Co. of Geneva, was purified by conversion into its hydrogen phthalate, and subsequently distilled. The pure alcohol (yield 40 per cent boiled at 118-120° (1 mm.), and was characterized by converting it into farnesal (semicarbazone, m. p. 125°), as recommended by Ruzicka.

Farnesol (10 g.) was heated with finely powdered potassium bisulfate, under 12 mm. pressure, in a flask placed in a bath maintained at 160-170°, the hydrocarbon being allowed to distil as it was formed. The product was a yellow oil, which, on redistillation over sodium, boiled at 127-130° (12 mm.) and had $d_{4^\circ}^{19.5^\circ}$ 0.8469 and $n_D^{19^\circ}$ 1.4945, with a yield of 4.7 g.

A portion of this dehydration product (1 cc.) was converted into bisabolene by heating it with 90 per cent formic acid (2 cc.) at 120-130° for 15 minutes. The product, when isolated, was an oil, b. p. 130° (15 mm.), which, when treated with dry hydrogen chloride in ethereal solution, gave the hydrochloride. This, when once recrystallized from methyl alcohol, gave the correct m. p. (79°) for bisabolene trihydrochloride. Another portion (0.1004 g.) was hydrogenated in acetic acid (Adams's catalyst) and took up an amount of hydrogen (37.8 cc. at N.T.P.) corresponding to $|\overline{\overline{3.5}}$ per $C_{15}H_{24}$.

Reduction, hydrogenation, and hydrochlorination of dehydration product.—A portion of the dehydration product (3.4 g.) was dissoved in absolute alcohol

(30 cc.) and reduced vigorously with lump sodium (9 g.). When ebullition slackened, the reaction vessel was heated on a water-bath, and more alcohol (50 cc.) was added. The product, isolated in the usual way and distilled over sodium, was an oil; b. p. 120-130° (12 mm.), d_4^{20} 0.8348, $n_D^{22°}$ 1.4786. Another portion (0.1854 g.), when hydrogenated as above, absorbed hydrogen (58 cc. at N.T.P.) corresponding to $|\overline{\overline{2.85}}$.

A third portion (1 cc.) was dissolved in dry ether, and saturated with dry hydrogen chloride at 0°. The crude hydrochloride (m. p. 50-56°) was fractionally crystallized from methyl alcohol, and so gave a less soluble hydrochloride, m. p. 77°, and a more soluble one, m. p. 49-41°. The former, when mixed with authentic bisabolene trihydrochloride (m. p. 79°), gave m. p. 77°, and the latter, when mixed with the trihydrochloride of the hydrocarbon derived by dehydration of dihydronerolidol (see above), gave the m. p. 50-51°.

Bromide of dihydrofarnesene.—Samples of dihydrofarnesene, derived (1) by dehydration of dihydronerolidol and (2) by reduction of the farnesene-bisabolene mixture from farnesol, were dissolved in chloroform and treated with slight excess of bromine in chloroform at 0°, and subsequently at room temperature. The bromides were unsolidifiable thick oils.

Synthesis of Squalene Hexahydrochlorides

Grignard Derivative from 1,4-*Dibromobutane.*—1,4-Butyleneglycol, derived from ethyl succinate[16], was converted by hydrogen bromide into 1,4-dibromobutane[16], and thence into the corresponding dimagnesium halide under von Braun and Sobecki's conditions (*loc. cit.*) as modified by Young, Prater and Winstein[8] to avoid the formation of considerable yields of dimeric and trimeric products.

To magnesium (8.64 g.), covered with dry ether, 1,4-dibromobutane (38.4 g.), dissolved in ether (80 cc.), was very slowly added with rapid stirring. Refluxing occurred, and when it subsided, more ether (150 cc.) was added, and the whole heated on a water-bath to refluxing for 0.5 hour. Little of the magnesium remained, and the Grignard complex separated out as a heavy oil.

Dihydroxydihydrosqualene.—Geranylacetone (46 g.; $\frac{2}{3}$ of theory), dissolved in ether (50 cc.), was added gradually, with good stirring, to the foregoing Grignard derivative. Refluxing set in, and the reaction was completed by maintaining gentle ebullition on a water-bath for 45 minutes. The greenish product was decomposed by cautious addition of water, and the crude glycol so formed extracted from the aqueous liquor (without acidification) with ether. The ethereal extract, dried over potassium carbonate, yielded a light yellow oil (40 g.), which gave by distillation under 1 mm. pressure the fractions: (1) b. p. 80-175°, 13.4 g.; (2) b. p. 220-250°, 24.1 g.; and (3) brown, semisolid residue, 2 g. Fraction (2) was a nearly colorless, somewhat viscous oil, which, on redistillation at 1 mm. pressure, gave a colorless oil, b. p. 220-235° (18 g.), and a more viscous liquid, b. p. 240-250°, which was rejected. The former, *dihydroxydihydrosqualene* (Found: C, 80.35; H, 12.3. $C_{30}H_{54}O_2$ requires C, 80.7; H, 12.2%), had $d_{4°}^{20°}$ 0.9079, $n_D^{20°}$ 1.4944, $[R_L]_D$ 143.2 (Calc.: 141.7); active H, 0.42 (Calc.: 0.45%); the latter appeared to be a mixture containing a little dihydroxydihydrosqualene and a similar substance probably derived from the C_8-Grignard derivative.

Squalene hexahydrochlorides.—Through dihydroxydihydrosqualene (5 g.), dissolved in dry ether, cooled in ice-salt and protected from moisture, a slow stream of dry hydrogen chloride was passed until the gas began to escape freely, and

then for a further 15 minutes. The solvent and excess of hydrogen chloride were removed at reduced pressure, whereupon the residue soon crystallized. The white crystalline mass (m. p. 100-120°), after being washed with ether, had chlorine content 33.8 per cent (Calc. for $C_{30}H_{56}Cl_6$: 33.7%). This was separated into three isomeric hexahydrochlorides, m. p.'s 107°, 112-115°, 144°, by the procedure of Heilbron *et al.* (*loc. cit.*): the isomerides (respectively) showed no depression of m. p. when mixed with the corresponding derivatives of similar m. p. obtained for comparison by treatment of genuine squalene from shark oil (*Symnorhinus lichia*) with hydrogen chloride.

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SUMMARY

A synthesis for dihydrofarnesene, $H \cdot [CH_2 \cdot CMe{:}CH \cdot CH_2]_3 \cdot H$, has been devised which appears to be capable of utilization in the formation of other low-molecular dihydropolyisoprenes, $H \cdot [CH_2 \cdot CMe{:}CH \cdot CH_2]_n \cdot H$, in which the individual isoprene units are uniformly arranged in head-to-tail fashion. This synthesis, starting from geraniol, gives a triene hydrocarbon which differs in one of its additive properties from a product described as dihydrofarnesene in the literature. The reason for the difference has been investigated.

A new synthesis for squalene has been devised which appears to be capable of utilization in the formation of other symmetrical dihydropolyisoprenes, $H \cdot [CH_2 \cdot CMe{:}CH \cdot CH_2]_n \cdot [CH_2 \cdot CH{:}CMe \cdot CH_2]_n \cdot H$, of the squalene type. This starts from geranylacetone and the Grignard derivative from 1,4-dibromobutane.

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STATISTICAL THERMODYNAMICS OF RUBBER. II *

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INTRODUCTION

During recent years, considerable progress has been made in connection with theories of rubber elasticity. Two general types of theories have been advanced, one from a macroscopic point of view and the other from a molecular point of view. An example of the former is the theory of Mooney,[1] who arrived at an equation which agrees well with observation. For molecular theories, the reader is referred to the work of Guth and Mark[2], Kuhn[3], and Pelzer[4], who carried through calculations of a statistical nature[5].

More recently, the author[6] extended the statistical theory along lines which avoided some of the earlier difficulties. In the present paper, the calculations will be carried still further, and the molecular theory will be related to the macroscopic theory of Mooney. It will also be shown theoretically that, although rubber does not obey Hooke's law for ordinary elongation, it should obey Hooke's law for shear.

It will be supposed that individual rubber molecules are long chain hydrocarbons capable of assuming various lengths and shapes as a result of free rotation about carbon-to-carbon valence bonds. When a piece of rubber is under no stress, the rubber molecules have a certain distribution of shapes. When the rubber is subjected to a stress, however, the molecules assume another distribution of lower probability. The theory here advanced relates this probability to the entropy of strain, thus providing a means of arriving at the mechanical properties of rubber.

Two postulates are made. (1) When a macroscopic piece of rubber is strained, the components of the lengths of the individual molecules (along some set of axes) change in the same ratio as does the corresponding dimension of the piece of rubber. (2) When a piece of rubber is elongated, no change in total volume takes place. The first assumption was made in the earlier paper of this series[6], whereas the second was not. Experimental support for the second postulate has been given by Holt and McPherson[7]. Our first problem is to investigate the effect of this second assumption on the equation of state for rubber.

STATISTICAL CALCULATIONS

Consider a cylindrical piece of rubber of length l_0 and diameter d_0 in its unstretched condition (Figure 1). If this piece of rubber is stretched so that its length is increased by a factor α, then the diameter must change by a factor $1/\sqrt{\alpha}$ in view of postulate (2). Within the piece of unstretched rubber, the molecules might appear as illustrated in Figure 2. Let x, y, and z equal the components of the distance between the ends of a molecule along the directions indicated (z values being measured perpendicular to the plane of the paper). Then, according to postulate (1), when the rubber is stretched along its length

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by a factor α, all of the x values increase by that factor and the y and z values change by the factor $1\sqrt{\alpha}$.

If the rubber molecules are uniformly long, the probability of finding a molecule with x, y, and z values in the range x to $x+dx$, y to $y+dy$, and z to $z+dz$ will be given by:

$$p(x, y, z)dxdydz = \frac{\beta^3}{\pi^{\frac{3}{2}}} \times \exp\left[-\beta^2(x^2+y^2+z^2)\right]dxdydz \tag{1}$$

for the unstretched configuration. In expression (1), β is a constant which depends on the number of atoms in the molecular chain and the distance between adjacent atoms. For convenience, let us change expression (1) to cylindrical coördinates (x, r, ϕ), where $r^2=y^2+z^2$ and $\tan \phi = z/y$. Then (1) becomes:

$$rp(x, r, \phi)dxdrd\phi = \frac{r\beta^3}{\pi^{\frac{3}{2}}} \times \exp\left[-\beta^2(x^2+r^2)\right]dxdrd\phi. \tag{2}$$

Intergrating over the angular coördinate, we obtain:

$$2\pi rp(x, r)dxdr = \frac{2\beta^3 r}{\sqrt{\pi}} \exp\left[-\beta^2(x^2+r^2)\right]dxdr \tag{3}$$

for the probability of finding molecules with x and r values in the ranges x to $x+dx$ and r to $r+dr$.

When the rubber is stretched, distribution (3) will be changed to:

$$2\pi rp'(x, r)dxdr = \frac{2\beta^3 r}{\sqrt{\pi}} \times \exp\left[-\beta^2(x^2/\alpha^2+\alpha r^2)\right]dxdr, \tag{4}$$

where $\alpha = l/l_0$. The problem now is to determine the probability of finding the system with distribution (4) when its most probable distribution is given by Equation (3).

To accomplish this, let us first divide the configuration space into elements of size $2\pi r_i \Delta r_i \Delta x_i$, each element being located in the neighborhood of r_i and x_i. Let s_i, equal the number of molecules in the ith cell and p_i equal the probability of finding a molecule in that cell. Also let $n_i = Np_i$ be the most probable number of molecules to be found in the ith cell, N being the total number of molecules. If P_0 is the probability of finding the system with its most probable distribution, and if P is the probability of finding it with some other distribution characterized by s_1, s_2, s_3, etc., then:

$$\ln (P/P_0) = \Sigma_i s_i \ln (n_i/s_i). \tag{5}$$

Equation (5) was derived in the first paper of this series[6], and will now be used directly. In the present instance, the quotient n_i/s_i is obtained by dividing expression (3) and (4):

$$\frac{n_i}{s_i} = \frac{p(x_i, r_i)}{p'(x_i, r_i)} = \exp\left[-\beta^2 x_i^2(1-1/\alpha^2) - \beta^2 r_i^2(1-\alpha)\right]. \tag{6}$$

Hence:

$$\ln \frac{P}{P_0} = -\beta^2(1-1\alpha^2) \times \Sigma_i s_i x_i^2 - \beta^2(1-\alpha)\Sigma_i s_i r_i^2. \tag{7}$$

But $\Sigma_i s_i x_i^2 = N\langle x^2\rangle_{Av}$, where $\langle x^2\rangle_{Av}$ is the average value of x^2 for distribution (4). Likewise $\Sigma_i s_i r_i^2 = N\langle r^2\rangle_{Av}$, where $\langle r^2\rangle_{Av}$ is also calculated by use of (4). On integration it is found that $\langle x^2\rangle_{Av} = \alpha^2/(2\beta^2)$ and $\langle r^2\rangle_{Av} = 1/(\alpha\beta^2)$. Therefore:

$$\ln (P/P_0) = -N(\alpha^2-1)/2 - N(1-\alpha)/\alpha,$$

$$= -N(\alpha^2+2/\alpha-3)/2. \tag{8}$$

It can be established readily that P has its maximum value (equal to P_0) when $\alpha=1$.

The entropy change accompanying the stretch can now be written. Evidently:

$$S = k \ln (P/P_0) = -Nk(\alpha^2+2/\alpha-3)/2. \tag{9}$$

If the stretch is carried out isothermally, then the total energy of the rubber is unchanged, providing only free rotation effects are utilized in rear-ranging the molecules. Hence the work done on the rubber must equal $-T\Delta S$ or:

$$W = (NkT/2)(\alpha^2+2/\alpha-3). \tag{10}$$

The restoring force is given by $(\partial W/\partial l)_T$ which is:

$$f = (NkT/l_0)[(l/l_0) - (l_0 l^2]. \tag{11}$$

Equation (11)[8] differs from the corresponding equation derived without postulate (2)[6] only in that the term $(l_0/l)^2$ has replaced a term (l_0/l). At first glance, this may not appear to be a significant improvement, but there is reason to believe that Equation (11) is superior to the earlier form.

To show this, let us first rewrite Equation (10):

$$W = (G/4)E(\alpha) + (G/4)F(\alpha), \tag{12}$$

where

$$G = NkT,$$

$$E(\alpha) = \alpha^2 + 1/\alpha^2 + 2/\alpha + 2\alpha - 6, \tag{13}$$

and

$$F(\alpha) = \alpha^2 - 1/\alpha^2 + 2/\alpha - 2\alpha.$$

Equation (12) is identical with Mooney's equation[1], except that Mooney had a different coeficient for $F(\alpha)$ as follows:

$$W = (G/4)E(\alpha) + (H/4)F(\alpha). \tag{14}$$

Since Equation (12) is closer to Equation 14) than any other equation derived by statistical means, and since Equation (14) gives excellent agreement with observation[1], we see that the present theory is almost complete. Moreover, we have shown that the molecular and macroscopic theories are compatible. It will be recognized that $E(\alpha)$ and $F(\alpha)$ are, symmetric and antisymmetric respectively, with regard to replacing α by its reciprocal. If $H=G$ (as the present molecular theory predicts) then there will be no symmetry between extension and compression processes. On the other hand, if $H \neq G$, then compression will have some resemblance to extension as far as the work required is concerned. Accordingly, H/G is a measure of the asymmetry of compression and extension, as pointed out by Mooney. To get Equation (14) from the statistical theory, it would be necessary to introduce a perturbation which would add terms resembling an energy of compression to the energy of extension.

RUBBER SUBJECTED TO SHEAR

The statistical theory will now be extended to a treatment of pure shear. Consider a bar of rubber of square cross-section arranged so that the diagonals of the square lie on a pair of cartesian axes (Figure 3). Now let the rubber be sheared so that its cross-section becomes a rhombus of area equal to that of the original square. For such a process, no effect will be noticed in the z direction, so that direction will be disregarded.

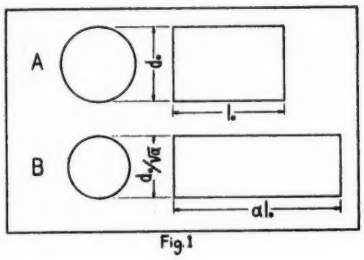

Fig. 1

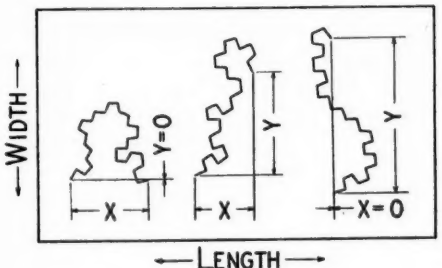

Fig. 2

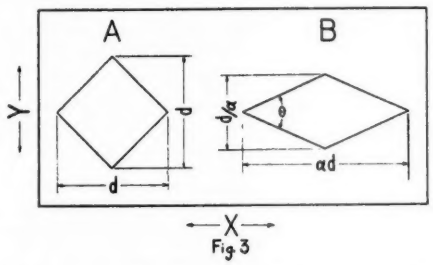

Fig. 3

FIG. 1.—A. Cylindrical piece of rubber in unstretched condition. B. Same piece of rubber after stretching.
FIG. 2.—Plane projections for rubberlike molecules.
FIG. 3.—A. Square cross-section of rubber before shear. B. Cross-section of same piece of rubber after pure shear of amount $\gamma = \alpha - 1/\alpha = [2(\csc\theta - 1)]^{\frac{1}{2}}$.

The original distribution of molecules with respect to x and y values will be:

$$p(x, y)\,dxdy = (\beta^2/\pi) \times \exp\,[-\beta^2(x^2+y^2)]\,dxdy. \tag{15}$$

After the shear, the distribution becomes:

$$p'(x, y)\,dxdy = (\beta^2/\pi) \times \exp\,[-\beta^2(x^2/\alpha^2+\alpha^2y^2)]\,dxdy, \tag{16}$$

assuming an extension in the x direction by a factor α. Substituting into Equation (5), there is obtained:

$$\ln\frac{P}{P_0} = \Sigma_i\, s_i[-\beta^2x_i^2(1-1/\alpha^2) - \beta^2y_i^2(1-\alpha^2)]. \tag{17}$$

Performing the indicated summation gives:

$$\begin{aligned}\ln\frac{P}{P_0} &= -N(\alpha^2-1)/2 - N(1-\alpha^2)/(2\alpha^2),\\ &= -N(\alpha^2+1/\alpha^2-2)/2.\end{aligned} \tag{18}$$

Hence:

$$W=NkT(\alpha^2+1/\alpha^2-2)/2. \tag{19}$$

But the amount of shear (γ) is measured by[9]:

$$\gamma=\alpha-1/\alpha. \tag{20}$$

Therefore:

$$W=NkT\gamma^2/2=G\gamma^2/2. \tag{21}$$

Equation (21) shows that rubber should obey Hooke's law with respect to shear, even if it does not obey Hooke's law for extension. The quantity G is called the modulus of rigidity.

DISCUSSION

One of the first points to be clarified is the significance of N, the total number of molecules. Assuming the validity of Equations (10) and (21), we must recognize that the apparent number of molecules depends on the state of vulcanization, because increased vulcanization increases G, the modulus of rigidity. Since vulcanization involves linking molecules together at various points, it is clear that N must be taken as the total number of molecular segments between linkage points, such points being regarded as the ends of the "molecules". The chain segments between such vulcanization bridges arrange themselves more or less at random, subject only to the condition that their ends are in fixed positions. The vulcanization bridges (or ends of "molecules") are assumed to respond to external constraints, in accordance with postulate (1).

From the foregoing discussion, it is seen that increased vulcanization increases the apparent number of molecules and hence the modulus of rigidity. If an experimental value for the rigidity is used to calculate a molecular weight by use of Equations (10) or (21), then the calculated molecular weight will be the average weight of the chain segments between points of vulcanization. Increased vulcanization decreases the "molecular weight" insofar as the concept of molecular weight is used in this theory.

The range of validity of the equations derived in this theory depends on the degree of vulcanization. A slightly vulcanized sample of rubber has long enough chain segments so that the probability distributions which were used are valid up to several hundred per cent elongation. On the other hand, a highly vulcanized sample has such short chain segments that the statistical arguments fail after a small amount of elongation. This follows because a short molecule is more likely to be found near its maximum length than is a long molecule. When an appreciable number of molecules approach their maximum lengths, then the external stretching force must become much greater than that predicted by Equation (11). This is in agreement with the findings of Gerke[10].

The prediction that rubber should obey Hooke's law for shear is particularly interesting. Mooney[2] quotes some unpublished results which directly confirm this point. On the basis of those experiments, Mooney assumed Hooke's law applying to shear as one of the postulates for his macroscopic theory.

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CONSTITUTION OF THREE-DIMENSIONAL POLYMERS AND THE THEORY OF GELATION *

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The peculiar properties of matter in the so-called gel state have inspired numerous theories pertaining to gelation and the structure of gels. Their low mobility has been attributed variously to the "brush heap" entanglement of highly elongated particles, to the solvation of large particles (solvated hull theory), or to the formation of network structures which extend throughout the volume, immobilizing entrapped liquid. About the only feature that these theories have in common is the recognition of the essential importance of very large particles or molecules. That these points of view are otherwise so divergent doubtless is due principally to the inclusiveness of the term gel. Consideration of the variety of substances classed as gels suggests at once that not all of these substances derive their properties from the same structural factors.

Heretofore, concepts regarding the phenomenon of gelation have been primarily qualitative in nature. The possibility of quantitative formulation of the conditions necessary for gelation and the description of the composition of gels according to a quantitative theory might appear to be remote, in view of the complexity of such systems. However, in certain cases these problems are amenable to statistical treatment. Systems in which molecules or particles are joined together at random to form network-type molecules, *e.g.*, three-dimensional polymers, or aggregates have been investigated recently from this point of view[1]. Equations have been derived expressing the critical conditions for infinite network formation. The compositions of certain types of three-dimensional polymers have been expressed as functions of the degree of chain branching or of cross-linking of the chains. Further applications of this theory to polymeric systems containing three-dimentional network structures will be discussed in this paper.

CRITICAL CONDITIONS FOR GELATION

It is a well-established rule that polymerizations which are propagated through the intermolecular reaction of bifunctional molecules lead to soluble, fusible products, whereas incorporation of units of higher functionality permits formation of gelled, or insoluble products. Thus, the polymer formed from the reaction of a glycol with a dibasic acid is soluble, regardless of the extent to which the interesterification reaction is carried, *i.e.*, regardless of the average molecular weight of the product. If a portion of the glycol is replaced by a trihydric alcohol, *e.g.*, glycerol, the reaction leads ultimately to gelation. In polymerizations of this type, structures such as that shown in Figure 1 are formed. Through further intermolecular condensations, such a process is functionally capable of producing an infinite network, *i.e.*, a network structure,

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the extent of which is limited only by the volume of the reaction mixture. Gelation of three-dimensional polymers is doubtless due to such macrostructures.

It has been shown that the rate of reaction of a functional group attached to a polymer molecule is uninfluenced by the size of the molecule[2]. Hence, in a three-dimensional condensation polymerization of the type depicted in Figure 1, the probability that any particular A group has undergone condensation is equal to the fraction of the A groups which have reacted, a quantity which can be measured experimentally. The probability, α, that a chain leading from a trifunctional unit (Figure 1) eventually leads to another branch unit can be expressed in terms of the fraction of the A groups which have reacted, the fraction of the B groups which have reacted, and the proportion of trifunctional units. The probability of the other alternative, *i. e.*, that the chain leads eventually to an unreacted terminal group, is $1-\alpha$. If $\alpha<\frac{1}{2}$, the indefinite expansion of a network is impossible, as a given chain has less than an even chance of reproducing two new chains. If $\alpha>\frac{1}{2}$, branching of successive chains may continue the network indefinitely. Hence, $\alpha=\frac{1}{2}$ represents the critical condition for incipient

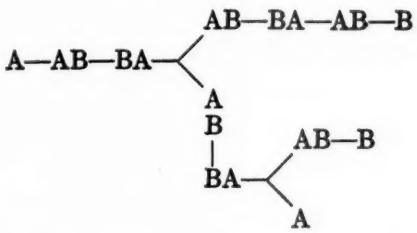

FIG. 1.—Trifunctionally branched polymer. A—A and B—B represent bifunctional units; A—$\lessdot^{A}_{A}$ represents the trifunctional branch unit. AB or BA is the product of the condensation of two functional groups.

formation of infinite structures[3]. All of the material will not be combined into "infinite molecules" when $\alpha>\frac{1}{2}$; as long as $\alpha<1$, finite termination of a network is possible. When $1>\alpha>\frac{1}{2}$, finite molecules will coexist with the infinite networks[4].

When the branching units are tetrafunctional, according to the same line of reasoning, the critical value of α is $\frac{1}{3}$. In general[3]:

$$\alpha_c=1/(f-1) \tag{1}$$

where f is the functionality of the branching units interpolymerized at random with bifunctional units.

The kinetics of gas-phase chain reactions which may undergo branching provide a close analogy with the circumstances in three-dimensional polymerizations[5]. If the probability of termination of the chain $(1-\alpha)$ exceeds the probability of branching (α) with reproduction of two chain carriers, the chains will be of finite length, and the rate of reaction will attain a finite steady-state value. If the probability of branching exceeds the probability of termination, the reaction will accelerate without limit, and an explosion will be observed. This analogy between gelation and certain gas-phase explosions can be carried further. A very slight alteration of temperature or pressure is sufficient to cause a gas-phase chain reaction, accompanied by branching, to accelerate from a moderate (or even negligible) rate to explosion. Similarly, a very small change in the total number of intermolecular linkages may change a three-dimensional polymer from a moderately viscous liquid to a gel having infinite viscosity.

In developing the statistical theory of three-dimensional polymers[1], it has been assumed, in order to simplify the problem, that no intramolecular linkages are formed in species of finite sizes; *i.e.*, it has been assumed that species of finite size are devoid of cyclic structures formed through reaction between two functional groups belonging to the same molecule. Experimental evidence[6] indicates that a small but appreciable fraction of the linkages in three-dimensional polymers are intramolecular. Consequently, gelation is observed[3] in three-dimensional polyesterifications at slightly higher extents of reaction than those calculated from the statistical theory in its present state of development. The discrepancy is comparatively small, and the measure of agreement with the calculations provides confirmation of the theory.

COMPOSITION OF THREE-DIMENSIONAL POLYMERS

In contrast to the deduction of the critical conditions for gelation, statistical derivation of equations expressing the relative quantities of species of various complexities is a more difficult mathematical problem. So far, solutions have been obtained for two cases: (1) bi- and trifunctional units joined together

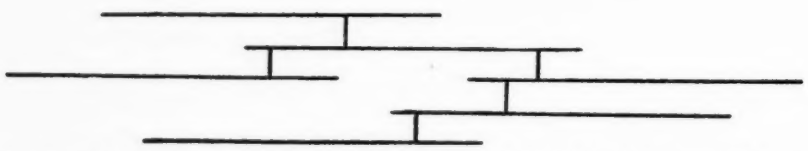

FIG. 2.—Randomly cross-linked chains of uniform length. Vertical lines indicate cross-linkages between chains, represented by straight lines.

randomly[4] (Figure 1), and (2) chains of uniform length randomly cross-linked at various points[7], as shown diagrammatically in Figure 2. This latter case may be regarded as a case of tetrafunctional branching, a cross-linkage and the units in each chain to which it is directly attached constituting the equivalent of a tetrafunctional unit. Although the mathematical methods employed in the two cases have little in common, the forms of the resulting distribution equations are strikingly similar[8].

For the case of cross-linked chains of uniform length[7], the weight fraction of molecules composed of z chains (z finite) is given by:

$$W_z = \frac{z^{z-1}}{\gamma z!}(\gamma e^{-\gamma})^z \qquad (2)$$

where γ, the cross-linking index, is defined as the number of cross-linked units in the entire polymeric mixture divided by the total number of chains. The degree of cross-linking, or the average number of cross-linkages per chain, is given by $\gamma/2$, since two cross-linked units are involved in each cross-linkage. In Figure 3 the weight fractions of molecules composed of one, two, three, four, and six chains are plotted against γ. At all stages of the cross-linking process, W_z decreases rapidly as z increases; chains unaffected by the introduction of cross-linkages are always present in greater quantity than any other species.

The summation ΣW_z over the weight fractions of all finite species, as given by Equation 2, is equal to unity[7] when $\gamma \leqq 1$. But when $\gamma > 1$, this sum becomes less than unity and equal to:

$$W_s = \gamma'/\gamma \qquad (3)$$

where γ' has the value, less than unity, such that $\gamma' e^{-\gamma'} = \gamma e^{-\gamma}$. That is, when $\gamma > 1$, a portion of the polymer given by:

$$W_g = 1 - \gamma'/\gamma \tag{4}$$

is not included in any of the species of finite size. This portion W_g represents the weight fraction of gel. The weight fraction of sol is given by W_s, and $\gamma = 1$ represents the critical point, or gel point, at which formation of infinite networks set in. The weight fraction of gel calculated from Equation 4 is included in Figure 3. The abruptness with which a gel makes its appearance in three-dimensional condensation polymerizations, *e.g.*, in the reaction of penta-

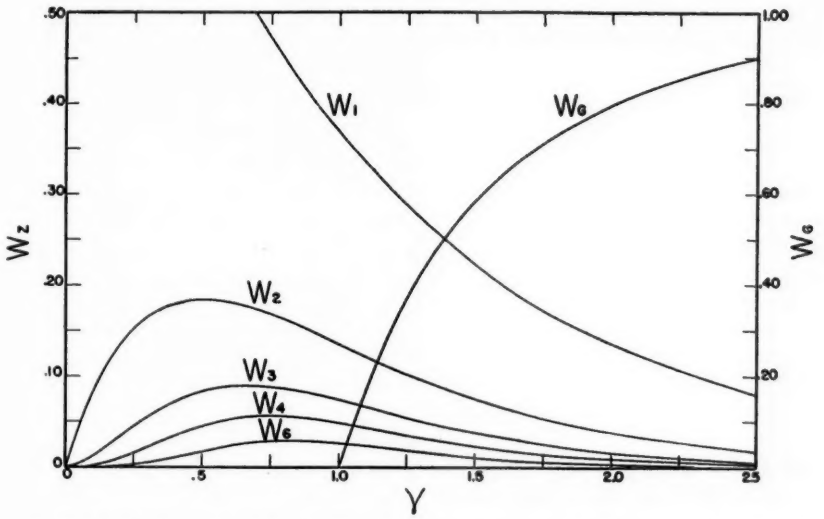

FIG. 3.—Weight fractions (W_z, left ordinate scale) of species composed of one, two, three, four, and six chains *versus* cross-linking index γ. Weight fraction of gel W_g (right ordinate scale).

erythritol with adipic acid[3], is significantly in accord with predictions of the statistical theory.

The quantity γ' represents the cross-linking index of the sol fraction alone. It follows from Equation 2 that, as γ is increased beyond unity, the composition of the sol fraction reverts over the same course traversed before gelation, γ' decreasing from 1 to 0. It can be shown that the cross-linking index γ'' for the gel fraction is given by $\gamma'' = \gamma + \gamma'$. At incipient gelation, $\gamma' = \gamma = 1$, and $\gamma'' = 2$, *i.e.*, the cross-linking index of the gel fraction (present in infinitesimal quantity) is twice that of the sol. After formation of gel has commenced, introduction of additional cross-linkages not only increases the quantity of gel at the expense of sol, but γ' decreases while γ'' increases. In other words, the disparity between the degrees of cross-linking in the sol and gel fractions increases as γ (for the polymer as a whole) increases beyond unity.

This situation is closely analogous to vapor-liquid equilibria. At the critical temperature (analogous to the gel point), the concentrations in the two phases are identical. As the temperature is lowered, the densities of the two phases diverge; the density of the condensed phase increases, while the density of the vapor decreases. Sol-gel transformations (of the type considered in this paper)

differ in that the two fractions are completely interspersed macroscopically. Nevertheless, the structural demarcation between the sol and gel fractions is as sharp as that between a liquid and its saturated vapor. The proportion of the material which could be considered as intermediate in complexity between sol and gel is negligible[9].

A corresponding treatment of the distribution of species in a polymer composed of cross-linked chains of nonuniform length would be much more difficult. For a distribution of chain lengths equivalent to that obtained by random coupling of bi- and tetrafunctional units, the critical point, according to Equation 1, is reached when $\gamma=\frac{1}{2}$ (which corresponds to $\alpha=\frac{1}{3}$). Thus, nonuniformity of the chains reduces the critical value of γ. It is not anticipated that other conclusions drawn above will require serious modification for application to the cross-linking of nonuniform chains.

AVERAGE MOLECULAR WEIGHTS

Attempts to evaluate molecular weights of three-dimensional polymers may yield highly deceiving results. End-group determinations or measurements of the colligative properties of polymer solutions yield the number average molecular weight $\bar{M}_n$, which may be defined as the weight of the sample divided by the total number of molecules. Up to the gel point, and somewhat beyond, the decrease in the number of molecules brought about by chain branching or by cross-linking is not large[8]. At the gel point, M_n may be of the order of twice what it would have been in the absence of chain branching or cross-linking. The observation of moderate values of $\bar{M}_n$ just before gelation has led to the erroneous conclusion that no very large species can be present in the gelled polymer[10]. Its inverse dependence on the total number of molecules makes M_n most sensitive to lower species, a small fraction of substance of very high molecular weight having almost no effect on this average.

Molecular-weight determination by either of the two known viscosity methods, —the dilute solution method of Staudinger[11] or the melt viscosity method developed recently by the writer[12],—yields the weight average molecular weight[13] $\bar{M}_w$[14]. This average is most sensitive to the high-molecular-weight fractions in the polymer, and is affected relatively little by components of very low molecular weight. Although these viscosity methods can be applied quantitatively only when the molecules are linear, it is safe to presume that approximate $\bar{M}_w$ values, correct at least within a factor of two or three, will be obtained with soluble three-dimensional polymers.

The statistical theory shows that $\bar{M}_w$, unlike $\bar{M}_n$, approaches infinity as the gel point is approached. Thus, the colligative and the viscosity molecular weights will be extremely divergent in this vicinity. Neither of these averages is properly indicative of the polymeric state of such substances; the number average is determined largely by fractions of low complexity, and the weight average is dominated by the components of greatest complexity. Determination of both averages would be desirable. In any case, an average molecular weight of a randomly branched or cross-linked polymer must be interpreted with caution.

Polymers which have passed beyond the gel point can scarcely be characterized adequately by an average molecular weight, as a portion of the substances possesses essentially infinite molecular weight. However, it should be possible to define the polymeric state of such substances in terms of two fundamental quantities: (1) the number of branch units, or of cross-linkages, per chain, and

(2) the number average chain-length, or chain molecular-weight. From a determination of the weight fraction of gel, *e.g.*, by extraction of sol[15], the former quantity can be determined, using Figure 3, for example, in the case of cross-linked chains of uniform length. The statistical theory then yields the degree of cross-linking in the sol fraction (γ'), which, in combination with $\bar{M}_n$ for the sol, yields the average chain length.

APPLICATIONS TO RUBBER

Recently Kemp and Peters[16] have shown that rubber films carefully prepared from fresh ammonia-preserved latex possess a sol fraction (petroleum ether-soluble) of only 10 per cent or less, but that the amount of sol increases on exposure to oxygen. This they attribute to rupture of the chains by oxygen. The larger sol fractions obtained by other investigators[17] they attribute likewise to partial oxidative degradation of the rubber prior to examination.

The presence of a gel fraction in raw rubber is believed to be due to occasional cross-linkages between the polyisoprene chains of the rubber hydrocarbon, which cause formation of networks[18]. The statistical theory makes clear that, if these concepts of the structure of raw rubber are correct, the division of rubber into two discrete fractions, sol and gel, of (almost) the same chemical composition is a natural consequence of random cross-linking of the long rubber chains. Experimental difficulties encountered in the sol-gel separation may, of course, obscure the sharpness of the distinction between the two fractions.

Overlooking for the moment that the polyisoprene chains in rubber are not of uniform length[19], for $W_g=0.9$ the value of γ is about 2.5 (see Figure 3) according to Equation 4; *i.e.*, the latex rubber films prepared by Kemp and Peters would contain about 1.25 cross-linkages per chain. As degradation by oxygen proceeds, γ decreases and the gel fraction decreases accordingly. Presumably, the chains are ruptured by oxygen at random. The decrease in γ, therefore, is due to an increase in the number of chains, while the total number of cross-linkages remains very nearly constant.

Osmotic-pressure molecular weights ($\bar{M}_n$) of soluble raw crepe rubbers determined by Meyer, Wolff, and Boissonnas[20] and by Gee[19] yield values in the vicinity of 300,000. For the sol fraction from an almost completely soluble crepe sample, Gee obtained $\bar{M}_n=340{,}000$[17]. Allowing for the effects of cross-linkages (about one per two or three chains), the number average chain molecular weight should be about 200,000[7]. However, if, before the osmotic-pressure measurements, degradation has decreased the gel fraction from about 0.9 to near zero, the original chain molecular weight must have been at least 2.5 times this value. Qualitative consideration of the effects of nonuniformity of the chains on these deductions would suggest a higher value,—perhaps 600,000 to 1,000,000, or a degree of polymerization of about 10,000 isoprene units per chain.

The concentration of cross-linkages estimated in this way is roughly one per 8000 structural units,—an exceedingly low figure.

PROTEIN GELS

Dilute aqueous solutions of certain proteins yield thixotropic gels under suitable conditions. Recently Myers and France[21] have investigated the behavior of egg albumin in aqueous solutions containing acetic acid. The increase in viscosity which follows addition of acetic acid is attributed by them to

gradual uncoiling of the protein chains. In the presence of small amounts of salts, the increase in viscosity is greatly accelerated, the viscosity proceeding to infinity with the formation of a thixotropic gel.

Interactions between amide groups are known to be very large, probably owing to the formation of hydrogen bonds[22]. If one adopts the view that a small number of hydrogen bonds may be formed between the dissolved protein chains, the gelation of protein solutions can be readily explained in the light of the network theory. The total number of amide-amide hydrogen bonds must eventually reach an equilibrium value which depends on pH, temperature, protein concentration, solvent medium, etc. The proportion of the bonds which are intramolecular, and therefore do not contribute to increasing the state of aggregation of the protein chains, are enhanced by the low protein concentration. It is assumed that, at equilibrium, the protein chains are completely uncoiled, except for the randomly distributed intrachain amide-amide interactions.

When the number of intermolecular hydrogen bonds exceeds one per 576 peptide linkages, there being 288 peptide units per albumin molecule, infinite networks will be formed. These networks will pervade the entire volume of the solution, giving to it the rigidity which places it in the classification of a gel. According to macroscopic observation, the solvent, *e.g.*, water and acetic acid in the work of Myers and France[21], is immobilized by a small proportion of protein.

A stress applied to the gel will tend to shift the equilibria governing the concentration and allocation of hydrogen bonds. In particular, a few interchain hydrogen bonds strategically located in networks of the gel fraction will bear the brunt of the stress. Considering the exceedingly small number of these bonds, it is evident that the stress required to rupture the infinite network structures will be quite small, especially when γ is but little greater than the critical value. The solution then will have acquired the properties of a fluid. When the stress is removed, the hydrogen bonds will reform in statistical distribution, and the solution will revert to a gel.

This sort of an explanation of thixotropy is by no means new[21], but with the aid of the statistical theory it is possible to understand more fully the changes which occur during mechanical destruction of the gel structure. The theory emphasizes that the fraction of the chemical structure which must be altered is exceedingly small.

It should be pointed out further that, in a gel structure involving interchain hydrogen bonds, the cross-linkages continually form and dissociate. Even in the quiescent state, the gel structures will be rearranging on a microscale; networks form and disintegrate in a state of dynamic equilibrium.

INORGANIC GELS

The present theory of gelation should be applicable, in principle, to inorganic three-dimensional polymers, *e.g.*, silicic acid gels[23], which are believed to be formed through intermolecular removal of water from orthosilicic acid molecules. Such processes unquestionably proceed at random, although all hydroxyl groups probably are not equally reactive. It may be necessary to assign different reaction probabilities to hydroxyl groups attached to silicic acid residues having one, two, three, and four unreacted hydroxyl groups. Quantitative tests of the theory are beyond prospect here, until methods are established for measuring these processes.

SUMMARY

In three-dimensional polymerizations, gelation is due to the formation of network structures of indefinite extent. These giant structures make their appearance when the degree of branching or cross-linking of the polymer chains exceeds a critical value. Gelation may be considered analogous to explosion in gas-phase reactions propagated by chains which undergo branching. After gelation has occurred, the sharp distinction between gel and sol is analogous to the demarcation between a liquid and its saturated vapor.

Observed average molecular weights of three-dimensional polymers must be interpreted with extreme caution, owing to the peculiarity of the distribution of species in the vicinity of the gel point.

Applications of the theory to raw rubber, protein gels, and inorganic gels have been discussed.

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THE EFFECT OF TEMPERATURE AND SOLVENT TYPE ON THE INTRINSIC VISCOSITY OF HIGH-POLYMER SOLUTIONS *

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According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in first approximation only on the volume concentration and the shapes of the suspended particles. By suitable application of such hydrodynamic considerations to solutions of long-chain molecules, it is possible in a rough fashion to derive the Staudinger-Kraemer equation, denoting proportionality between specific or intrinsic viscosity and molecular weight. It is an experimental fact, however, that the proportionality constant, K_m, depends not only on the type of polymer concerned, but also on the temperature and the nature of the solvent. Even in the dilute range, where specific viscosity is linear with concentration, these variations are often quite considerable. This paper tries to treat such variations in a systematic fashion, and to advance for them an explanation which is based on changes in the average geometrical shape of the particles. A relationship between intermolecular and intramolecular agglomeration tendency is presented.

THEORETICAL CONSIDERATIONS

According to various investigators[1], a long-chain hydrocarbon molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and the rigid linear configuration assumed by Staudinger[2]. Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains, but the configurations of intermediate extension predominate statistically. The average or effective value of any shape-dependent molecular property (such as hydrodynamical influences) may be obtained by summing this property over all configurational states, after each state has been given a proper weight factor. If the long chain molecule is surrounded by a continuous, energetically indifferent solvent, then the weight factor for a particular configuration is determined only by internal parameters—potential energy function for restricted rotation, prohibition of segment interpenetration, etc. The mean value of any molecular property in such an indifferent (and perhaps hypothetical) solvent might be called the "unbiased" statistical mean for the property.

If the solvent is energetically unfavorable, so that the dissolving of the high polymer is an endothermic process, then the polymer segments attract each other in solution and squeeze out the solvent between them. The curling forces in such a case will be similar to those postulated in the Mack[3] theory of rubber elasticity. Those molecular configurations which involve many contacts of the molecule with itself are weighted more heavily than in an indifferent solvent,

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and the mean value of any molecular property represents a more curled and contracted shape than the unbiased mean. On the other hand, if a solvent is energetically more favorable than the indifferent solvent, as previously defined, then in solution the long chain molecule will be surrounded by a solvated hull which tends to prevent polymer-polymer contacts. Uncurled configurations is favored, and the mean value of any property represents a more extended shape than the unbiased mean. Since an extended or uncurled configuration is associated with a high intrinsic viscosity, and *vice versa*, the first prediction as to effect of solvent type on viscosity is the following.

Other conditions being equal, a given high polymeric material made up of flexible molecules exhibits a high intrinsic viscosity in an energetically favorable solvent, and a low intrinsic viscosity in an energetically unfavorable solvent. This, of course, holds only for very diluted systems. At higher concentrations (around or above 5 per cent by weight) an energetically unfavorable solvent favors polymer-polymer contacts between different chains and hence leads to the danger of gelation, while an energetically favorable solvent stands a higher concentration of the polymer and yet gives a fluid, stable solution. Solvents are often classified as "good" or "bad" on the basis of the viscosity of concentrated solutions.

If a good solvent is mixed with a precipitating agent, the resulting mixture can be expected to be energetically less favorable to a long chain molecule than is the pure solvent. A dilute solution of high polymer in a solvent-non-solvent mixture should, therefore, exhibit a lower intrinsic viscosity than a solution of the same polymer in the pure solvent. It will be shown that a series of high polymer solutions of given polymer concentration, in mixtures of increasing nonsolvent content, shows a regular decrease in specific vicosity until the precipitation point is reached.

We have interpreted variations in the intrinsic viscosity of a given high polymeric material as being due to changes in the degree of intramolecular agglomeration. If this interpretation is correct, there should be also a close connection between the intrinsic viscosity of a high polymer solution and the degree of intermolecular agglomeration. Exactly the same solvent characteristics which determine the mean geometrical properties of an isolated long chain molecule should also determine the amount of association of different solute molecules into aggregates. When a nonsolvent is added to a high polymer solution, the point at which precipitation begins represents a certain definite agglomeration tendency for chain segments of different molecules. To a first approximation, therefore, it should represent a certain definite mean value for any shape-dependent internal property. That solvent composition which is critical from the standpoint of solubility should correspond to a certain intrinsic viscosity, no matter what the solvent and what the nonsolvent. One would therefore conclude the following: The intrinsic viscosities of a series of solutions of a given polymer in solvent-nonsolvent mixtures of increasing nonsolvent content, should decrease to a final value at the limit of solubility. This final value should be in first approximation the same in all solvent-nonsolvent systems.

All these effects should be more pronounced for polymer molecules of high flexibility than for more rigid chains. A paraffin chain should exhibit greater shape changes than a cellulose derivative.

The effect of temperature on intrinsic viscosity should depend strongly on the nature of the solvent. In a poor solvent, the effective molecular shape is

more compact and curled than the unbiased statistical mean. An increase of temperature should increase the relative importance of entropy factors over energetic factors, and result in an uncurling of the molecule. In such a solvent, a temperature increase should result in an increase of intrinsic viscosity. In a very good solvent, the energetic weighting factors favor the more extended configurations; here a temperature increase should result in a downward approach to the unbiased statistical mean shape. In a very good solvent, therefore, a temperature increase should cause a decrease in intrinsic viscosity. There should be an intermediate case in which the intrinsic viscosity is independent of temperature over a limited range.

The above use of the "unbiased statistical mean" as the shape which is approached as the temperature increases is an oversimplification, since this value itself includes energetic weighting factors, arising from the internal potentials of the molecule. If we consider only the forces which depend on the solvent,

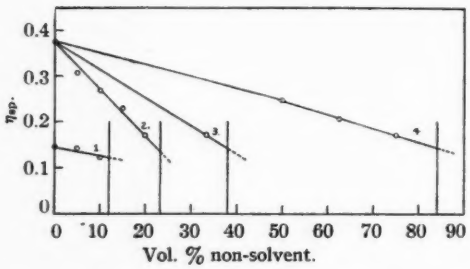

FIG. 1.—Variation of specific viscosity of 0.2% polystyrene solutions with nonsolvent content: (1) methylethyl ketone-methanol; (2) toluene-methanol; (3) toluene-isoamyl alcohol; (4) toluene-acetone.

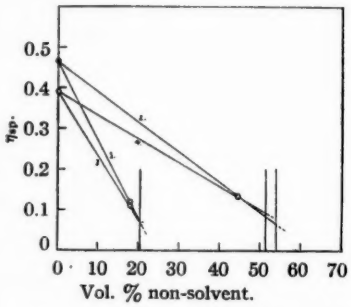

FIG. 2.—Variation of specific viscosity of 0.0468% rubber solutions with nonsolvent content: (1) carbon tetrachloride-methanol; (2) carbon tetrachloride-acetone; (3) toluene-methanol; (4) toluene-acetone.

we can make the prediction that in a very good solvent, the intrinsic viscosity of a dilute solution of a flexible polymer should decrease with temperature; in a poor solvent, it should increase.

EXPERIMENTAL

Polystyrene, rubber, and cellulose acetate were used in this investigation. The polystyrene had a weight average molecular weight of 165,000, calculated from viscosity data, and using a K_m value of 1.1×10^{-4}. The rubber was smoked crepe, with a weight average molecular weight of 223,000, based on a K_m value of 2.7×10^{-4}. The cellulose acetate was a fraction with a molecular weight of 35,000, which had been obtained by Harris and Sookne from a sample of commercial cellulose acetate having a weight average molecular weight around 90,000.

Solutions of polystyrene at a concentration of 0.2 per cent by volume in the following solvent-nonsolvent systems were investigated: Methylethyl ketone-methanol, toluene-acetone, toluene-methanol, toluene-isoamyl alcohol. Figure 1 shows the variation of specific viscosity with nonsolvent content. In each case, the specific viscosity decreases as the mixed solvent become less favorable,

until the coagulation point is reached. For all the solvent-nonsolvent systems investigated, the specific viscosity at the solubility limit is in the same range.

Solutions of rubber at a concentration of 0.0468 per cent by volume in the following solvent-nonsolvent systems were investigated: toluene-methanol, toluene-acetone, carbon tetrachloride-methanol, carbon tetrachloride-acetone. Figure 2 shows the variation of specific viscosity of these solutions with composition of the mixed solvent. Rubber behaves in the same general way as polystyrene.

Solutions of cellulose acetate at 0.2 per cent by volume in the following solvent-nonsolvent systems were investigated: methylcellosolve-methanol, acetone-methanol, acetone-toluene. The specific viscosities of all solutions were about 0.33. The nature of the solvent medium apparently had no marked effect on the shape of the cellulose acetate molecule in solution. It is to be expected that the cellulose chain is much less flexible than the rubber and polystyrene molecules.

TABLE I

η_{sp} AS A FUNCTION OF TEMPERATURE

Sample	Temperature (°C) 25	60
Rubber in		
Toluene	0.390	0.373
Carbon tetrachloride	0.466	0.430
Toluene—14% methanol	0.205	0.243
Polystyrene in		
Toluene	0.370	0.350
Toluene—10% methanol	0.320	0.317
Toluene—20% methanol	0.160	0.185
Toluene—10% amyl alcohol	0.336	0.340
Toluene—33% amyl alcohol	0.170	0.210

EFFECT OF TEMPERATURE

Viscosities of many of the solutions were determined at two different temperatures, 25 and 60° C. Table I shows the relation between the specific viscosity at 60° C and that at 25° C, as a function of solvent composition, for several systems. In the pure solvents, specific viscosity decreases with temperature, while in the mixtures containing much nonsolvent, specific viscosity increases with temperature.

EFFECT OF CONCENTRATION

The effect of concentration on specific viscosity (in the dilute range) was investigated in both "good" and "poor" solvents, and at different temperatures. A sharp molecular weight fraction of polystyrene (mol. wt. 730,000) was used in this part of the investigation.

If η_{sp} is given by a power series in concentration, there will be a range in which all terms but the first can be neglected ($\eta_{sp}=ac$). Experimentally this range turns out to be very small in the case of a high molecular-weight sample. Deviations from the simple linear relation are found at concentrations well below 0.05 per cent by volume. For a somewhat wider range, the first two terms will serve to give the viscosity: ($\eta_{sp}=ac+bc^2$). Experimentally, this range proves to be fairly wide, even for high molecular weight samples. When η_{sp}/c

is plotted against c, the slope of the straight line gives the second coefficient, b, and the ordinate intercept gives the first coefficient, a. In Figure 3 (η_{sp}/c) is plotted against c for polystyrene in toluene, and a mixture of 80 per cent toluene and 20 per cent methanol. In this way is seen the effect of temperature and solvent type on both virial coefficients. The presence of the nonsolvent not only reduces the linear coefficient (which reflects the shape of individual molecules), but also reduces to an even greater degree the second coefficient (which is determined by the degree of interaction among different molecules).

An increase in temperature shifts the whole curve downward in the case of toluene, and upward in the case of the toluene-methanol mixture. In the toluene-methanol mixture, the interaction term, b, is least important at the lowest temperature.

It may be significant that Flory[4] has reported a similar situation in regard to the osmotic pressure-concentration relationship for high polymer solutions.

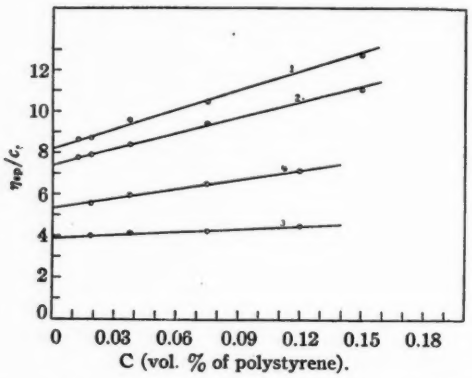

FIG. 3.—Relation between η_{sp}/c and c for polystyrene solutions: (1) toluene, 20° C; (2) toluene, 80° C; (3) 20% methanol, 80% toluene, 20° C; (4) 20% methanol, 80% toluene, 60° C.

The osmotic pressure is more nearly linear with concentration in "poor" solvents than in "good" solvents.

SUMMARY

1. The specific viscosity of a dilute solution of polystyrene or rubber is strongly dependent on the nature of the solvent; the specific viscosity is high in a good solvent, and low in a poor solvent or a solvent-nonsolvent mixture. This has been interpreted as being due to changes in mean molecular shape. The specific viscosities of cellulose acetate solutions are not so sensitive to the nature of the solvent.

2. The extrapolated specific viscosity at the limit of solubility is in the same range for several different solvent-nonsolvent systems.

3. The effect of a temperature increase is to lower the specific viscosity of rubber or polystyrene solutions in a good solvent, but to increase the specific viscosity in a mixture of solvent and nonsolvent.

4. The specific viscosity of a dilute polystyrene solution is more nearly linear with concentration in a toluene-methanol mixture than in pure methanol. The quadratic term b in the equation: ($\eta_{sp}=ac+bc^2$), is reduced relatively more than the linear term a by the presence of the nonsolvent.

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THE PLASTIC-ELASTIC BEHAVIOR OF EBONITE *

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The so-called plastic yield of ebonite, *i.e.*, its deformation at elevated temperatures, has been studied extensively because it limits the practical applications of the material, but these studies have hitherto suffered from the lack of a guiding hypothesis as to the mechanism of the process.

It has previously been shown[1] that the deformation characteristics of ebonite, and their variation with temperature, can be represented by a mechanical model comprising an elastic phase insensitive to temperature and a temperature-sensitive viscous or plastic phase. The object of the present paper is to show that the properties assigned to these phases arise not from two different materials but from different types of bond between the parts of the molecular network, the plastic characteristics being due to the relaxation of one type. This hypothesis is shown to explain the observed facts relating to the plastic-elastic behavior of ebonite.

While the hypothesis was being elaborated, there appeared translations of two papers[2] on the deformation of high polymers, including ebonite, in which the important part played by relaxation was emphasized, and certain conclusions reached identical with those indicated by the present hypothesis; these will be referred to in the appropriate sections. An earlier paper[3] is interesting because it describes in general terms the contrasting types of deformation shown by ebonite at normal and high temperatures, respectively.

The stresses and strains considered are all relatively small, and do not approach anywhere near the breaking point. Except where otherwise indicated, the discussion relates to well-vulcanized rubber-sulfur ebonites.

1. DEVELOPMENT OF THE HYPOTHESIS

(i) Rubber vulcanizates, including ebonite, consist of randomly kinked isoprene chains joined together into a 3-dimensional network by strong cross-links, probably sulfur bridges; these links, and the valency bonds in the chains, will be termed *primary bonds*. Adjacent parts of the network are normally held together also by cohesional (van der Waals) forces and perhaps also by entanglements, as postulated by Busse[4] and Treloar[5]; all these will be termed *secondary bonds*.

(ii) With rising temperature, the vibrational energy of the bodies joined by a bond increases until, at a critical energy, the bond becomes unstable, *i.e.*, it ceases to have any effective hold, and the bodies can be separated by a very small force. Secondary bonds become unstable at lower temperatures than primary bonds; thus, in ebonite the secondary bonds, though stable at room temperatures, are unstable at about 100° C, but the primary bonds are still substantially stable at this temperature.

(iii) It follows that, at and above about 100° C, the deformation of ebonite is wholly or mainly controlled by the primary network of isoprene chains and cross-

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links. In this temperature region Young's modulus is found[6] to be about 150 kg. per sq. cm., which is very much less than for ordinary amorphous organic solids, *viz.*, about 10,000-200,000 kg. per sq. cm. (Houwink[7]), but of the same order of magnitude as for soft vulcanized rubber, *viz.*, 15 kg. per sq. cm. This suggests that the high-temperature deformation of ebonite is a case of rubber-like elasticity, due to the mobility of the molecular chains and their tendency to assume a randomly kinked form by thermal agitation; this confirms the conclusion of previous workers[8] that ebonite exhibits high elasticity. The greater number of cross-links (? sulfur bridges), compared with soft vulcanized rubber, restricts the mobility and so leads to a higher modulus than for the latter.

(iv) At room temperatures, where the secondary bonds are stable, Young's modulus is very high[9] (20,000-25,000 kg. per sq. cm.) This must arise from the force required to strain these bonds, a conclusion consistent with calculated values for such forces in nonrubberlike organic polymers[10]. As unvulcanized rubber is much more easily deformable, the secondary bonds responsible for the high modulus of ebonite must be associated with the sulfur atoms, which are, indeed, known to exert relatively strong cohesional forces[11].

(v) In a solid containing a large number of similar bonds, the vibrational energies, at any given moment, of the bodies joined by them vary considerably from bond to bond, owing to the random transfer of energy from one body to another, these vibrational energies being distributed according to some frequency-distribution law (not necessarily the normal probability law). In general, therefore, a certain proportion of the bonds are unstable because the vibrational energy exceeds the critical value. Rise of temperature moves the frequency-distribution curve towards higher energy and so increases the proportion of unstable bonds, which must therefore be related to temperature by an integrated distribution curve of the general type shown in Figure 1 (temperature/stability curve).

(vi) The vibrational energy of the bodies joined by a given bond varies randomly with time, so that, by analogy with (v), the bond is sometimes stable and sometimes unstable. As the result of a statistical equilibrium, however, the number of bonds in the unstable state remains the same, and is purely a function of temperature, as shown in Figure 1.

(vii) During the periods of instability, separation of the bodies joined by the bond, and hence deformation of the structure as a whole, can occur under the action of an external force. Hence when a constant force is applied, the initial small instantaneous deformation, due to elastic straining of the bonds, is followed by progressive deformation (relaxation) due to the continual breaking of the secondary bonds as they become temporarily unstable; in the absence of any other controlling mechanism this deformation continues indefinitely. (Constancy of the number of unstable bonds is maintained by the formation of new bonds, made possible by the local molecular rearrangements.) If a constant strain is applied, the secondary bonds break one by one and reform in new positions; by this relaxation the originally strained bonds are gradually replaced by unstrained ones. The higher the temperature, and hence the less stable the secondary bonds as a whole (see Figure 1), the more rapidly will all these processes take place.

All time effects in the deformation of ebonite are thus due to relaxation arising from the continual breakage of secondary bonds under the influence of the external force, and the acceleration of these effects by rise of temperature is due to the increasing instability of these bonds.

2. DEFORMATION UNDER CONSTANT STRESS

Time/Deformation Curve

Figure 2 shows a typical set of curves for various temperatures, as determined by a torsion method[12]. At and below about 50° C, the deformation is very small, and becomes sensibly constant after a few minutes.

The continued upward slope of the curve for 105° C seems to be due to a slow drift superposed on the main deformation. This drift, which becomes more noticeable at higher temperatures, has not been fully studied, and will therefore not be further discussed.

The general form of the curves suggests that, at all but the lowest temperatures, the deformation would ultimately reach about the same limiting value, though the rate of approach varies greatly with temperature; Gurevich and Kobeko[13] give curves indicating the same conclusion. The limiting deformation is clearly that fixed by the elastic primary network. The rate of approach to it

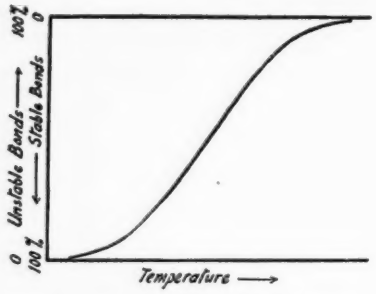

Fig. 1.—Temperature/stability curve.

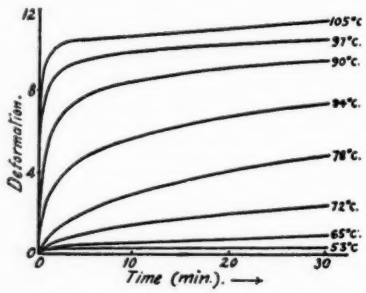

Fig. 2.—Time/deformation curves.

depends on the relaxation or breakdown of the secondary bonds, which is necessary to allow the material to deform, and is more rapid the higher the temperature. The quantitative relationship between temperature and rate of relaxation is discussed by Aleksandrov and Lazurkin[14].

Below about 50° C relaxation, if it occurs, is evidently too slow to be noticeable, and the observed small deformation is due to elastic straining of the secondary bonds.

The characteristic shape of the time/deformation curve is explicable by the theoretical deduction of Prandtl[15] that, when a body undergoes relaxation under the action of a constant force, the deformation increases with time as shown in Figure 3 (full curve). In ebonite, the primary network limits the ultimate deformation, so that the curve bends over and becomes practically horizontal (dotted curve). Aleksandrov and Lazurkin[14] derive an equation relating deformation with time and temperature. This gives time/deformation curves similar to those in Figure 2 except that they begin as straight lines from a point just above the origin; these authors also give experimental curves for soft vulcanized rubber at about −60° C, which are of this type. In the present author's experience, however, the curves for ebonite always show the initial concavity to the time axis which Prandtl's investigation predicts.

If ebonite is deformed to near the limiting deformation and then released, the time/recovery curve should theoretically be similar to the time/deformation curve, but inverted. The limited data available[6] agree with this.

Alternate Deformation and Recovery

Observations[6] on the behavior of the same specimen subjected to successive equal periods (30 minutes) of deformation under constant stress, separated by recovery period of varying length, are also in accord with the hypothesis. If the recovery between two stressing periods (OX and XY, Figure 4) were of infinitesimal duration, no relaxation could occur; hence the recovery, AB, would be very small, corresponding only to the elastic strain in the secondary bonds, and the second time/deformation curve, BAC, would be substantially a continuation of the first (OA). With an infinitely long recovery period, recovery would be complete and the second curve would be an exact repetition of the first. Experimental results agree with these predictions in that, with short recovery periods, *e.g.*, 5 minutes, the behavior approximates the first case, but approaches more nearly the second case as the recovery period is made longer.

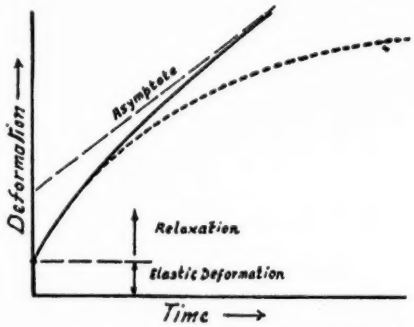

Fig. 3.—Theoretical time/deformation curve.

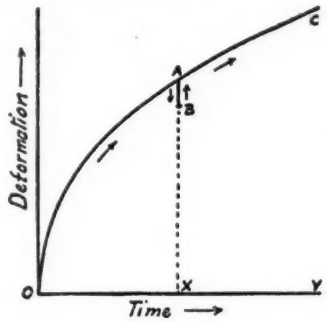

Fig. 4.

Temperature/Deformation Curve

The relation between deformation after a fixed stressing period (normally 30 minutes) and temperature will now be considered. Apart from the very small elastic strain observed below about 50° C, deformation always depends on relaxation and, hence, on the proportion of unstable bonds. It must therefore increase with temperature, much as shown by the temperature/stability curve, Figure 1, but eventually reaching the limit set by the primary network. Experiments show this to be the case, except that the drift referred to above makes the limit rather indefinite (Figure 6 gives experimental curves for various ebonites). Similar curves have been deduced[14] from a theoretical equation relating deformation of high-elastic materials with time and temperature.

3. RESIDUAL STRAIN (SET) AFTER DEFORMATION

The hypothesis requires that at all temperatures recovery should ultimately be complete, given sufficient time, because, if relaxation of the secondary bonds occurs, the elastic primary network can restore the original shape, and if there is no relaxation, the deformation must be elastic and reversible. Under conditions where recovery is relatively quick, *i.e.*, at room temperatures and at about 100° C, ebonite has been found to recover to within less than 1 per cent of the applied deformation[16]. The deformation of synthetic (butadiene) rubber ebonite is said[18] to be fully reversible at all temperatures between −40° C and +160° C.

After short recovery periods, however, the residual strain (set) may be considerable. This has been studied by Church and Daynes[1], who measured the set after a fixed torsional strain, the straining and recovery periods being normally one and two minutes, respectively. With increasing temperature, the set passed through a maximum (curve E, Figure 5). The existence of a maximum has been explained by Gurevich and Kobeko[13], but the shape of the temperature/set curve can be more fully explained as follows:

When the specimen is strained for a short period, relaxation of the secondary bonds occurs to an extent which varies with the temperature, as shown by curve X, Figure 5 (similar to Figure 1); at the highest temperature it is complete, so that only the primary network remains stressed. When the specimen is released, the stresses in this network, in their attempt to restore the original shape, have to break down the new secondary bonds resulting from the relaxa-

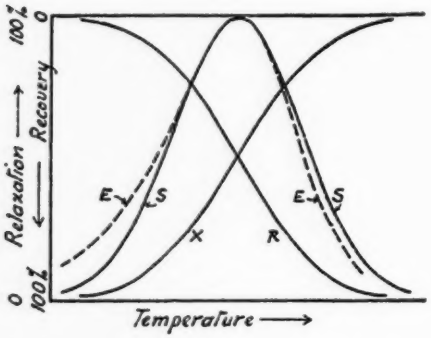

FIG. 5.—Derivation of temperature/set curve.

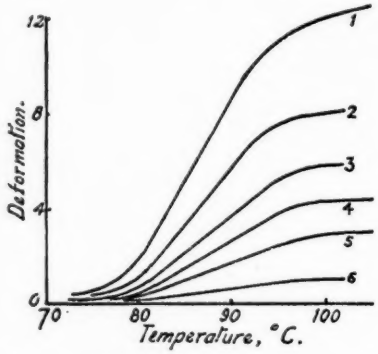

FIG. 6.—Temperature/deformation curves—1: Rubber-sulfur ebonite; 2-6: Ebonites containing fillers.

tion. The rate of this breakdown varies with temperature in the same way as the original relaxation, since it is, in fact, a relaxation in the reverse direction. The temperature/recovery curve R is, therefore, similar to curve X but inverted, so that the ordinate represents the fraction of these new bonds that remain unbroken after recovery. The set is determined by the number of these unbroken bonds which are trying to retain the strained shape. This number is given by the product of the ordinates of curves X and R, and so varies with temperature, as shown by curve S, which is seen to be closely similar to the experimental curve E.

The observation[1] that the set usually falls to practically zero at about 97°-98° C indicates that at this temperature, substantially all the secondary bonds are unstable.

Figure 5 shows that the peak of the temperature/set curve S should correspond to the middle of the relaxation curve X and, hence, to about the middle of the temperature/deformation curve, which has been shown (above) to be similar to the latter. This is found to be approximately the case[6], the observed small discrepancies being attributable to experimental errors and to differences in the test conditions, *e.g.*, stressing periods, used in measuring set and deformation, respectively.

A phenomenon allied to set is that of latent strain. If ebonite is deformed

when hot, and allowed to cool while held in the deformed shape, it retains this shape indefinitely but, if again heated, it reverts to the original shape. This behavior is due to the fact that, at room temperature, the secondary bonds do not relax and therefore do not allow the strained primary network to restore the original shape.

4. INFLUENCE OF VARIOUS FACTORS ON DEFORMATION AND SET

Periods of Strain and Recovery

Raising the temperature accelerates relaxation and is, therefore, qualitatively equivalent to lengthening the time; an equation deduced by Aleksandrov and Lazurkin[14] expresses the relationship quantitatively. By lengthening the time, a given effect can thus be produced at a lower temperature, so that, for instance, the temperature/deformation curve and the peak of the temperature/set curve should be shifted in the direction of lower temperature. The following data show that this is so.

(*a*) *Temperature/Deformation Curve*[17] (other data[2] indicate similar effects)

Stressing period (min.)	0.5	1	2	10	30	60	120	300	1380
Movement of curve (°C) relative to 0.5-min. curve	0	−1.5	−3	−6	−8.5	−9	−10	−11	−12.5

(*b*) *Peak of Temperature/Set Curve*[1]

Straining period (min.)	1	10	1	10
Recovery period (min.)	0.25	0.25	2	2
Peak temperature (°C)	70	66.5	67.5	65

Degree of Vulcanization

Increasing vulcanization introduces more sulfur atoms and, hence, more of the relatively heat-stable secondary bonds associated therewith. The secondary bond system as a whole thus becomes more stable, so that the temperature/stability curve (Figure 1) moves in the direction of higher temperature, resulting in a corresponding movement of the temperature/deformation curve and of curves X and R and, hence, the temperature/set curve S, in Figure 5. Experiments confirm that an increase in either the proportion of sulfur or the vulcanizing period causes the predicted movement of both temperature/deformation and temperature/set curves[18].

Gurevich and Kobeko[13] attribute the slower relaxation of more fully vulcanized ebonites to the growth of macromolecules, as a result of which each molecule is held by a greater number of cohesional bonds, and so has its movements restricted. It is very doubtful, however, whether separate molecules exist in ebonite, so that this explanation seems less satisfactory than the one here advanced, depending on the strong cohesional forces associated with the sulfur atoms.

Increasing vulcanization would be expected also to stiffen the primary network by introducing more cross-links, thus reducing the limiting deformation, *i.e.*, the maximum height of the temperature/deformation curve. This effect has been observed in some experiments[17] but not consistently; data for a synthetic rubber ebonite vulcanized to various degrees[13] illustrate the effect very clearly.

Incorporation of Plasticizer

Incorporation of increasing proportions of mineral oil moves both the temperature/deformation and temperature/set curves progressively in the direction of lower temperature[6]. This can be ascribed to the relatively weak cohesional forces known[11] to be characteristic of hydrocarbon groups. Thus, if an oil molecule lies between two parts of the ebonite network that would otherwise be held together by the normal secondary bonds, these will be replaced by the weaker and less heat-stable bonds between the hydrocarbon groups of the oil molecule and the network. The heat-stability of the secondary bond system is therefore lowered, and the characteristic curves are thus displaced in the direction of lower temperature.

Aleksandrov and Lazurkin[14] record a similar effect on the temperature/deformation curve as the result of incorporating a plasticizer into a methyl methacrylate polymer.

Incorporation of Ebonite Dust

Ebonites made from mixes containing ebonite dust, *i.e.*, previously vulcanized ebonite, finely ground, have been found to exhibit two peaks on the temperature/set curve[1]. This is because the dust particles remain as a separate disperse phase, which is more highly vulcanized than the matrix of newly formed ebonite. Each of these phases produces its own peak at the appropriate temperature, so if they differ sufficiently in degree of vulcanization, the two peaks are clearly distinguishable on the resultant curve.

Incorporation of Fillers

A rubber-sulfur ebonite at high temperature resembles a soft vulcanized rubber at room temperature, in that their elastic moduli are of the same order of magnitude, *viz.*, about 150 and 15 kg. per sq. cm., respectively. The pronounced stiffening effect which fillers exert in soft rubber should, therefore, be observed also in ebonite at high temperatures. The following data show that this is so, deformation under a given stress being reduced to about the same extent as in soft rubber, compare columns (i) and (ii).

	Deformation, relative to "blank"		
Filler (percentage by volume of mix)	(i) Soft rubber at room temperature	(ii) Ebonite at 105° C	(iii) Ebonite at room temperature
Nil (blank)	1.00	1.00	1.00
Magnesium carbonate, 9.5%	0.56	0.48	1.09
Magnesium carbonate, 21.5%	0.29	0.22	0.65
Magnesium carbonate, 34%	0.14	0.10	0.40
Amorphous silica, 16%	0.42	0.36	0.75

The figures in column (ii) relate to the upper end of the temperature/deformation curve, where the primary network is the controlling mechanism. At lower temperatures, where deformation is largely governed by relaxation, the filler must again reduce the deformation, but whether in the same proportion as indicated above is difficult to predict. Experiments show that the reduction is approximately proportionate over the steeply rising and upper flat parts of the curve, so the effect of the filler is essentially to reduce the vertical scale. This

is seen in Figure 6, relating to ebonites made by adding various fillers to the same rubber-sulfur mix.

At still lower temperatures, *e.g.*, at room temperature, where there is no appreciable relaxation and the rubber-sulfur ebonite itself has a very high modulus, fillers would be expected to have less stiffening effect, since in the hypothetical extreme case where the ebonite has the same modulus as the filler, incorporation of the latter would have no effect. This is confirmed by the data in column (iii) above, which show that the fillers have relatively less effect on deformability at room temperature than at 105° C.

Synthetic (Butadiene) Rubber Ebonites

Ebonites made from butadiene polymers (Buna-85 and Buna-115) show much less deformation at high temperatures than natural rubber ebonites[19]. This can be ascribed to the absence of the lateral methyl groups in the butadiene polymer chains. Hydrocarbon groups possess relatively weak cohesional forces[11], so the introduction of one such group into every butadiene-sulfur unit (approximately C_4H_6S) must reduce the average strength of the cohesional (secondary) bonds and, hence, the heat-stability of the whole structure. Many analogous cases can be found among low-molecular organic compounds, where introduction of a methyl group often lowers the melting-point considerably.

SUMMARY

A hypothesis is put forward to explain the plastic-elastic behavior of ebonite and its dependence on temperature. This is based on the previously described mechanical conception of ebonite as a system comprising a heat-stable elastic phase and a viscous temperature-sensitive phase, but the difficulty of reconciling this two-phase concept with the probable structure of ebonite is avoided by replacing the elastic and viscous phases respectively by primary and secondary (cohesional) bonds, the relaxation of the latter, due to their relatively low temperature-stability, being responsible for all time effects in the deformation of ebonite.

The hypothesis explains the main facts relating to so-called plastic yield and to the residual strain after recovery from deformation, and thus appears to form a useful basis for further research on ebonite.

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RUBBER PHOTOGELS *

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Gels formed by the action of light on rubber solutions in the absence of oxygen have been called photogels by Stevens[1]. This name may be misleading unless it is realized that it refers only to the mode of production, and does not imply any chemical similarity between these substances. Similar substances can be produced without the action of light, and photogels may show as wide chemical differences as heat vulcanizates (thermogels) made with different vulcanizing agents.

Porritt[2] was the first to record this phenomenon, but the first systematic attempt to study photogels was made by Pummerer and Kehlen[3], who came to the conclusion that "the gel formation was perhaps an effect similar to vulcanization, but was brought about by polymerization." Pummerer emphasized the importance of the study of rubber photogels as a possible means of elucidating the mechanism of vulcanization. In the following year a practical paper by Novotny[4] appeared on the photogelation of rubber cements. This author suggested that the gelation was probably due to vulcanization brought about by traces of sulfur in the hydrocarbon solvents and traces of chlorine spit off from the carbon tetrachloride solvent. Two years later Meyer and Ferri[5] showed that photogels could be produced under conditions which rigorously excluded oxygen. This led to the conclusion that the cross-linking had taken place, not by means of oxygen bridges, but by means of direct linkages between double bonds which had been activated by light. In the following year Spence and Ferry[6] repeated in a somewhat modified form the work of Pummerer and Kehlen[3], and extended it to the action of light on latex[7]. Spence and Ferry put forward the view that in both enhanced polymerization and degradation the rubber is oxidized: in the one case presumably by dehydrogenation and in the other with the introduction of oxygen. More recently Stevens[1] has reviewed the whole field of photogels in a paper in which he largely disagrees with the observations and conclusions of Pummerer and Kehlen[3]. The present author has in turn been unable to confirm some of the observations of Stevens; the work has, however, shown that most of the phenomena connected with photogelation are in line with our present concepts of the rubber molecule.

(1) FORMATION OF PHOTOGELS

(a) GENERAL

Photogels can be formed by the action of diffused light on rubber solutions, in the absence of oxygen, in common glass containers. Ultraviolet light is not essential, although gel formation is more rapid when the light from a mercury arc is employed and the rubber solution is enclosed in a quartz vessel. The solvent may or may not combine with the rubber during gel formation. Repre-

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sentative solvents of the two classes are benzene or cyclohexane and carbon tetrachloride. These solvents have been employed throughout the work described in this paper. Another characteristic of photogelation is that, for every set of conditions, there is a limiting degree of gelation beyond which it is impossible to proceed, whatever the length of irradiation. Even with the optimum conditions of choice of solvent, activator, source of light, etc., it is impossible to obtain a final product, after removal of solvent, which, from the point of view of sulfur-vulcanization evaluation is more than very lightly vulcanized.

(b) Effect of Oxygen

(i) *On gel formation.*—When a rubber solution is exposed to light in the presence of excess of oxygen or air, the oxygen is slowly absorbed, and the viscosity of the rubber solution decreases to a limiting value[8]. In the presence, however, of insufficient oxygen, the viscosity falls until all the oxygen has been absorbed; thereupon gelation commences, provided the degree of degradation has not been too great for the particular gelling conditions, *i.e.*, nature of solvent, concentration of activator, etc. Confirmation of this fact was obtained by breaking tubes of alkaline pyrogallol in the vessels at different degrees of irradiation. Unlike the initial degradation with its steady decrease in viscosity, gelling is not attended by a uniform increase in viscosity, but takes place with production of stringiness. The effect of oxygen is to delay gelling, and the larger the amount of oxygen, the greater the delaying action and the weaker the resulting gel, measured by the weight required to produce a given distortion with a loaded ball. Benzene solutions are much more sensitive to the initial proportion of oxygen than carbon tetrachloride solutions in the absence of higher concentrations of activator. Thus, although a 5 per cent solution of rubber in benzene containing 1 per cent of benzophenone (on the rubber) will gel in the course of a few days, a similar solution in the presence of an equal volume of air will not gel even after prolonged exposure. A similar solution in carbon tetrachloride will gel in the course of a few hours, but, in the presence of an equal volume of air, gelling will take place, although it will take three to four times as long. In the presence of 5 per cent of activator, the effect of air is still greater on the gelling of benzene solutions. Thus, the benzene solution will take about eight times as long to gel in the presence of an equal volume of air, whereas, in the case of the carbon tetrachloride solution, the time is only doubled.

In view of the conclusions of Meyer and Ferri[5], attempts were made to demonstrate that photogels could not be produced in the complete absence of oxygen and to prove that the cross-linking obtained in their experiments could have been derived from the oxygen milled into the rubber during its mastication. In these experiments the unmasticated rubber was prepared in an atmosphere of nitrogen from latex saturated with oxygen-free nitrogen. It was dried in nitrogen and sealed with the necessary amount of cyclohexane (which had just previously been distilled in a current of nitrogen) to give a 5 per cent solution in a tube, the bottom end of which was quartz and the upper end ordinary glass. No activator was employed. Before sealing, the tube was cooled in solid carbon dioxide and methanol, and washed out several times with purified nitrogen by the aid of a vacuum pump. Solution of the rubber in the sealed tube was effected by heating the tube for two hours at 200° C in an autoclave filled with cyclohexane. The resulting solution gelled in 3 hours when placed 15 centimeters from a 1000-watt mercury quartz lamp, with air cooling. A solution made from the same

rubber, after light mastication with free access of air, required 16 hours to gel. By submitting the solution of the masticated rubber to heat treatment similar to that given to the unmasticated rubber, the time required to gel was increased. There is little doubt, therefore, that the most careful exclusion of oxygen tends to accelerate gelling; nevertheless this fact cannot be accepted as evidence of cross-linking by activated bonds, since it might equally well have taken place through the few already-existing oxygenated centers in the rubber molecules.

(ii) *On reversion of the gel.*—Photogels revert to solutions when exposed to further irradiation in the presence of oxygen. Although gel formation with certain exceptions, *e.g.*, Neoprene gels, takes place throughout the volume of irradiated solution, reversion takes place progressively from the surface in contact with oxygen or air. Photogels in carbon tetrachloride are much more stable than those in benzene and take longer to revert. In this behavior, photogels resemble gels obtained by the treatment of rubber solutions with sulfur chloride. Both types of gels of similar rigidity take roughly the same time for photoreversion. Another similarity between photogels and sulfur chloride gels it that, after complete reversion, the final solutions have the same viscosity, whether made from lightly or heavily milled rubber[9]. Provided degradation has not gone too far, it is possible to regel the reverted solution by further irradiation in the absence of oxygen. Thus, a stiff gel made from lightly masticated rubber with little initial oxygen and reverted by the appropriate amount of oxygen can be regelled by further irradiation in the absence of oxygen. Reverted weaker gels obtained from highly masticated rubber, or those produced with a larger amount of initial oxygen, or reverted stronger gels which have been too degraded by too long irradiation in the presence of too much oxygen, cannot be regelled without the addition of a further quantity of an activator.

In general, it is more effective from the point of view of both speed of regelling and strength of the gel to add a further quantity of activator after reversion rather than to employ the same total concentration of activator at the beginning of the first gelling. Thus with a 5 per cent rubber solution in benzene with a 2 per cent of benzophenone (on the rubber) it was found impossible to regel the reverted solution (14 days' exposure for reversion) by further irradiation but, by the addition of 1 per cent more of benzophenone to the reverted solution (14 days' exposure) of a gel containing 1 per cent benzophenone, regelling was effected after 40 days' further exposure.

(c) Effect of Solvent

Solvents can be divided into active solvents, which condense, and inactive, which do not condense with rubber. Those which condense with rubber, such as carbon tetrachloride, are more reactive, and gel formation is more readily effected. Gelling in such solvents is less easily influenced by activators and retarders, and the gels thus formed are firmer and more stable to reversion. Furthermore, gels can be formed from smaller rubber molecules or, in other words, more degraded rubbers which refuse to gel in inactive solvents gel in active solvents. Thus, rubber which has been "killed" by prolonged mastication (5 per cent solution with 1 per cent on the rubber of benzophenone as activator) takes seven times as long to gel as lightly masticated rubber in carbon tetrachloride, but similar rubber under similar conditions in benzene does not gel in fifty times the exposure required to gel lightly masticated rubber in that solvent.

(d) Activators

Pummerer and Kehlen[3] and Stevens[1] have made a special study of activators. In general, activators are well-known photosensitizers, such as aldehydes or ketones, *e.g.*, benzaldehyde, benzophenone, eosin, etc. Activators accelerate degradation as well as gelation. These substances either take part in the reaction or are destroyed, since the speed of gelling or reversion or regelling can be increased by addition of more activator at a later stage. Substances such as maleic anhydride, which are known to condense with rubber, will bring about more rapid gelling of a rubber solution in benzene by irradiation. The speed of gelation increases both in benzene and carbon tetrachloride with increase in concentration of activator (benzophenone) up to about 7 per cent on the rubber after which further increase in activator produces no further speeding of gel formation.

(e) Effects of Milling and Types of Rubber

In general, the smaller the rubber molecules in a given solution, the slower is gelling and the weaker the final gel. "Killed" rubber, or rubber first submitted to extreme oxidation by irradiation in the presence of oxygen, is difficult to gel unless comparatively large quantities of substances which condense with rubber (and are hence able to link together the small molecules) are present. Thus, provided sufficient oxygen is present at the outset of the irradiation, rubbers of different chain length all behave in the same way. Unmilled plantation crepe, dissolved in cyclohexane by the action of heat in the absence of oxygen, gells in a shorter time than a similar solution made from the same rubber lightly masticated. The unmasticated sol fraction of pale crepe gells in roughly the same time as the masticated rubber from which it is made, but the gel fraction, brought into solution by prolonged heating at a high temperature in the absence of oxygen, required seven times as long to gel. The sol fraction of a deproteinized latex appears to gel more rapidly than the sol fraction from ordinary latex.

(f) Effect of Antioxygens

Several authors have shown that antioxygens, *e.g.*, phenylnaphthylamines, accelerate the degradation of rubber solutions. The same antioxygens delay gelling, and the ultimate gels are weaker than those obtained in the absence of the antioxygen. In the presence of larger proportions of activator, the effects of the antioxygen are smaller. The antioxygen appears to have less effect when the initial amount of oxygen is greater. The presence of an antioxygen appears to have no delaying effect on reversion, and may even slightly accelerate it. The gel, reverted in the presence of an antioxygen, regels under conditions which do not bring about regelling in a gel reverted in the absence of such antioxygen. This points to the fact that, although the uptake of oxygen has been just as rapid or even more rapid, the ultimate particles (not necessarily straight chains) are larger than would be obtained in the absence of the antioxygen. This is in line with the results obtained by Johnson and Cameron[10], who showed that antioxygens have no effect on the increase in stretch necessary to produce a crystalline pattern after aging, although they help to maintain tensile strength. The antioxygens employed in the above work were of both the staining (amino) and nonstaining types (phenolic), since it was thought that the staining type might affect the results by the alteration in light absorption. An antioxygen has a far smaller effect on the gelling of rubber solutions in active solvents than in

inactive solvents unless a substance which condenses with rubber is present in the inactive solvent. Thus, in the absence of oxygen a 5 per cent rubber solution (with 1 per cent on the rubber of benzophenone) in carbon tetrachloride containing 1 per cent of nonstaining antioxygen on the rubber requires 3.5 times as long to form a gel, whereas in a corresponding benzene solution the delay caused by the antioxygen is of the order of 20 times, and even then the resulting gel lacks the firmness of that obtained in the absence of the antioxygen. The delaying action of the antioxygen is even more marked in the presence of oxygen.

Hydroquinone delays gelling. Both in the presence and absence of oxygen, 1 per cent of hydroquinone on the rubber in a 5 per cent solution in benzene in the presence of 1 per cent benzophenone prevents gelling after 50 times the exposure required to produce gelling in its absence. Stevens[1] found that hydroquinone accelerated gel formation in the presence of oxygen. Breitenbach, Springer and Horeischy[11] found that hydroquinone prevented almost completely polymerization of styrene in the presence of oxygen, but had little effect in its absence. The delaying effect is not so marked with rubber solutions in carbon tetrachloride. In the absence of oxygen, the time required for gelling is doubled; but in the presence of oxygen (10 per cent by volume on the solution) gelling requires 25 times the time required to effect gelling in the absence of hydroquinone. Under similar conditions, but adding the hydroquinone by breaking a sealed tube in the sealed container at the end of the degradation period, the solution requires only four times that required to complete gelation in its absence. The effect of sulfur is interesting. Porritt[2] claimed it prevented gelation; Stevens[1] that it caused little, if any, delay. Six per cent of sulfur was milled into pale crepe, and a 5 per cent solution of the product in benzene containing 1 per cent of benzophenone (on the rubber) was irradiated in the absence of oxygen. The solution became transparent, due to the complete solution of the sulfur, and there was a slight increase in viscosity, but gelation could not be effected after several months' exposure to summer sunlight.

(g) Effect of Proöxygens

Proöxygens delay or inhibit gelation. One per cent of copper oleate (on the rubber) in a 5 per cent rubber solution containing 5 per cent (on the rubber) of benzophenone doubles the time of gelation in the absence or presence of oxygen. One per cent of rubber "peptizing agents" (thionaphthols) prevent gelling, both in the presence and absence of oxygen. Even when extreme precautions are taken to eliminate oxygen from all the substances used in the experiment, it is impossible to form even a weak gel after prolonged irradiation.

(h) Effect of White Pigments

Fifteen parts of finely divided pigment were dispersed by ball-milling in a 5 per cent rubber solution containing 1 per cent (on the rubber) of benzophenone. The suspensions were exposed to daylight side-by-side.

Blank	5 days to form gel
Barium sulfate	2 " " "
Magnesium carbonate	3 " " "
Zinc oxide	8 weeks " "

The delaying action of zinc oxide was unexpected, since zinc oxide is known to be a photosensitizer[12].

(2) PROPERTIES OF PHOTOGELS

Photogels show all the properties of vulcanized or cross-linked molecules. Their most important characteristic is that, however long the exposure, their degree of vulcanization cannot be increased. They are but lightly cross-linked. Spence and Ferry[6] have already suggested that this may be due to the cross-linking being limited either to the ends of chains or to active hydrogen points. Therefore, on drying, they show very low tensile strength, which is of course to be expected from lightly cross-linked products. They exhibit all the usual characteristics of vulcanized products, such as insolubility, and resistance to flow at high temperatures[13]. Some pass through a stage of pseudo-photogelation, but this can be detected by the fact that such gels liquefy on warming or on treatment with a trace of a peptizing agent.

The solid products from photogels and reverted photogels have been prepared on a sufficiently large scale to submit them to the usual rubber technological evaluations. These results will be described in detail elsewhere, but it is sufficient to state here that they simulate the technological behavior of lightly vulcanized rubber and a very degraded reclaimed rubber.

(3) PHOTOGELS FROM SYNTHETIC RUBBERS

Most synthetic rubbers readily form photogels, which differ in certain respects from those obtained from natural rubber. Since all the synthetic rubbers have been mixed with antioxygens at the time of manufacture, it is essential for this work to free the commercial synthetic rubbers from antioxygens by prolonged wet milling with methanol.

The simple butadiene polymers, *e.g.*, Buna-85, gel more readily than natural rubber. The speed of gelation and the firmness of the gel are less influenced by the presence of oxygen. The gels do not revert when irradiated in contact with oxygen, and will often undergo syneresis, with separation of much firmer gels, which can be dried and which give higher tensile strengths than the corresponding gels from natural rubber. Antioxygens delay gel formation, and here again the delay is not greatly affected by varying amounts of oxygen.

The butadiene interpolymers, butadiene-acrylonitrile, *e.g.*, which have to be studied in a solvent mixture of benzene and methyl ethyl ketone (3:7), never really form solutions and do not readily form photogels. In general, larger proportions of activator have to be employed, and gel formation takes about twenty-five times longer than that with straight polymers. The resulting gels exhibit properties similar to those of butadiene polymers.

Some chloroprene polymers, *e.g.*, Neoprene-M, form gels, but not so readily as natural rubber. Gel formation with Neoprenes invariably takes place inwards from the wall exposed to light, whereas with natural rubber and simple butadienes, gel formation takes place through the mass simultaneously. Gel formation with this Neoprene is just as susceptible to the presence of oxygen as natural

	1% benzophenone			1% benzophenone 1% antioxygen			5% benzophenone			5% benzophenone 1% antioxygen		
	Full	0.75	0.5	Full	0.75	0.5	Full	0.75	0.5	Full	0.75	0.5
Rubber	2 Days	NG	NG	Weak 15	NG	NG	1	5	6	3	5	5
Buna-85	1	2	5	12	12	15	1	1	1	3	4	5
Neoprene M..	25	NG	NG	NG	NG	NG	3	11	27	20	20	23

rubber, *i.e.*, oxygen delays gelling. Neoprene-M gels often undergo syneresis, and do not revert when irradiated in the presence of oxygen. No photogels could be obtained with Neoprene-GN, which is known to contain sulfur. Photogels of solutions of synthetic rubbers in carbon tetrachloride, even in the presence of activators, could not be obtained after long exposures.

(4) THEORETICAL DISCUSSION OF GEL FORMATION

It is suggested that all samples of rubber contain at least one or more oxygenated centers per molecule which make condensation cross-linking possible by irradiation in the absence of free oxygen. In the presence of oxygen, the first effect is probably to produce hydroperoxides, which become the reactive centers for further attack by activated oxygen. In the presence of further oxygen, the effect is to produce an oxidation cleavage at these points, but as soon as the supply of oxygen is exhausted, cross-linking takes place by the activated condensation of the remaining hydroxyl groups. If the initial quantity of oxygen is too great, gel formation will not take place, either because of destruction of the potentially reactive hydroxylated centers, or because the resulting fragments are too small to link into a gel by cross-linking. In the case of solutions in active solvents, the solvent acts as the bridge by actual condensation with the rubber. Possibly both simple condensation oxygen bridging and active solvent condensation bridging take place simultaneously. Breitenbach, Springer and Abrahamczik[14] have shown, for example, that when styrene is polymerized in solution in carbon tetrachloride there is obtained, together with the simple polymer, a condensation product of styrene and carbon tetrachloride.

The behavior of synthetic rubbers is also in agreement with the above views. They are more stable to oxygen cleavage: hence gel formation is less affected by the presence of oxygen, and the resulting photogels do not revert. They also condense with carbon tetrachloride less readily, and hence do not form photogels in that solvent with the same ease as natural rubber.

C. W. Bunn has kindly made x-ray diffraction photographs of some of the dried gels. The only difference between the photographs of the rubbers before and after irradiation is a slight difference in the positions of the maximum intensity of the diffuse band: 4.7 before and 4.8-4.9 A. U. after treatment. Sulfur vulcanization does not normally shift the position of the diffuse band, and we are therefore forced to the conclusion that, in addition to the cross-linking, a small proportion of the rubber has probably been cyclized[15].

SUMMARY

1. The conditions of photogel formation and reversion in rubber solutions have been studied. The larger the rubber molecule the more readily is gel formation effected.

2. Photogels exhibit all the properties associated with cross-linked molecules.

3. Photogels made with most synthetic rubbers are not influenced to the same extent by the presence of oxygen, and do not revert on further exposure in the presence of oxygen.

4. The suggestion is made that gel formation is due to oxygen-bridging of already oxygenated centers. This bridging is not possible in the presence of oxygen, since further oxidation results, with cleavage of the molecule. In the case of active solvents, bridging may be due primarily to condensation with solvent. Bridging is also probably accompanied by a limited degree of cyclization.

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THE CAOUTCHOL COMPONENT OF NATURAL RUBBER

A CORRECTION *

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The author recently described a method[1], developed in Malaya, for separating natural rubber into two main fractions, one containing, among other things, a hydrocarbon which was called caoutchene; the other including an oxygenated substance which constitutes about 2-5 per cent of natural rubber. The latter, which was named caoutchol, was described as a nontacky, freely soluble, highly elastic substance, for which the formula $C_{80}H_{130}(OH)_2$ was suggested. Caoutchene, constituting 87-91 per cent of total rubber, and isolated only in a crude state, was described as tacky, of low tensile strength, and giving solutions of notably low viscosity, and its elongation under tension was stated not to exceed 200 per cent. It was further suggested that the elasticity of rubber was derived essentially from its minor component, caoutchol.

The author has now been able to examine again the substance, in collaboration with his colleagues on the staff of the British Rubber Producers' Research Association. Fresh facts have been brought to light, both here and elsewhere, in consequence of which it has been found necessary to amend or withdraw the suggestions originally put forward. Nevertheless it is emphasized that caoutchol is a naturally occurring substance of real interest, quite distinct from artificially oxidized rubbers.

A critical comment by Kraay and Altman[2] claims to show that caoutchol is an oxidation product of caoutchene; first, because increased access of oxygen gave increased yields of the caoutchol fraction, and secondly, because further amounts of the caoutchol fraction could be obtained by resubmitting the precipitated caoutchene to the fractionation procedure. Unfortunately, however, the authors made no attempt to characterize the material contained in the caoutchol fractions. They did not attempt to show that it was, in fact, caoutchol, and not caoutchol together with, for example, the somewhat differently constituted oxidation products of rubber hydrocarbon. Their conclusion, therefore, cannot be accepted as valid.

A further communication, by Haefele and McColm[3], pointed out that, if care were taken to exclude air, the removal of caoutchol from rubber did not lead to tackiness and loss of elasticity in the residual crude hydrocarbon. Their evidence, though strong, unfortunately suffers from lack of quantitative data.

Their observation is, however, supported independently by Gee and Treloar[4], who have shown that fractions of purified rubber hydrocarbon obtained by removal of gummy oxygenated substances from natural rubber are still highly elastic and similar in physical properties to total crepe rubber. Moreover, it has been shown by Treloar[5] that it is not necessary to postulate a two-phase system to account for the elasticity of natural rubber, and that such elasticity is essentially a property of the long-chain molecules of which rubber is composed. In the light of these publications, the author now withdraws his suggestion that

* Reprinted from the *Journal of the Chemical Society*, **1942**, pages 223-225.

the elasticity of rubber is derived essentially from that of its minor component caoutchol.

The author's claim that caoutchol purified by hydrolysis is a chemical individual, with a formula approximating to $C_{80}H_{130}(OH)_2$, must be withdrawn in the light of the following new evidence, for details of which the author is indebted to the workers named.

(1) Caoutchol, whether hydrolyzed or not, can be fractionated. G. F. Bloomfield, employing the technique previously applied to rubber by Bloomfield and Farmer[6], has obtained the following fractions:

Type of caoutchol	Light petroleum-acetone at 20° C	Percentage dissolved	Average molecular weight	Oxygen content (percentage)
Hydrolyzed	50/50 extract A	47	45,000	0.15
	50/50 extract B	16	—	0.1
	55/45 extract	23	93,000	1.6
	Residue (insoluble in light petroleum or in petroleum-acetone)	10	—	6.2
Unhydrolyzed	50/50	29.2	20,000	3.95
	52/48	14.6	53,000	1.3
	55/45	16.4		0.9
	60/40	32.2	70,000	1.05

(2) The molecular weight, as determined by G. Gee, does not agree with the molecular weight required by the formula. Molecular weights of four different samples, determined by viscosity methods already described[7], were 43,000, 47,000, 50,000, and 57,000. The molecular weights of the last two, determined osmotically, were 51,000 and 54,000. These high values cannot be ascribed to association, since the specific viscosity of the first sample in benzene was shown to be almost independent of temperature.

(3) The analytical evidence, by W. T. Chambers and F. Hilton, does not point unequivocally to the formula suggested (Found: C, 85.7, 86.5, 86.1, 85.3; H, 11.7, 12.0, 11.8, 11.2; OH 0.48[8]. Calculated for $C_{80}H_{130}(OH)_2$: C, 85.4; H, 11.8; OH, 3.0%).

Nevertheless, as has already been stated, caoutchol is a naturally occurring substance of considerable interest, differing markedly in physical properties from any artificially oxidized rubber which has been examined in these laboratories. In the first place, L. R. G. Treloar has shown that, in spite of its low molecular weight, caoutchol possesses mechanical properties approximating much more closely to those of total rubber than to those of a degraded rubber of approximately the same molecular weight. Using the methods already applied to rubber[9], Treloar has shown:

(*a*) That the maximum elongation of caoutchol is 700 per cent at 25°.

(*b*) That the tensions are only 20-40 per cent lower than those of crepe rubber at corresponding elongations.

(*c*) That the plastic flow at 25° is relatively small, being not more than 6 per cent of the elastic elongation (the corresponding figure for crepe rubber is 2 per cent).

(*d*) That crystallization of caoutchol commences at 400 per cent elongation and that its birefringence rises to 60 Na wave-lengths per mm. at the breaking point. The latter figure is about one-half the maximum observed in crepe rubber at the same elongation.

In contrast with this, both a rubber hydrocarbon and an artificially oxidized rubber of similar molecular weight (60,000) were observed to be merely sticky gums, without appreciable strength or elasticity. The possession of good rubber-like properties by the low-molecular caoutchol is thought to indicate a stronger cohesion between the molecules than occurs in the rubber hydrocarbon, at least at certain points in their length.

Furthermore, G. A. Jeffrey, over a period of time, has examined the x-ray diffraction patterns of a number of samples of caoutchol prepared in Malaya. He finds that, when stretched, all the samples give a well-defined fibre diagram identical with that of stretched rubber, but that in the unstretched state they show a diffraction pattern having a narrower halo than that of unstretched rubber and two or more distinct Debye-Scherrer rings. On freezing at 0.5° for several days, caoutchol does not give the powder diagram characteristic of frozen rubber. A summary of his observations on unstretched caoutchol is included in the following table of mean values for the glancing angles of the diffraction maxima. Figures in parentheses indicate the number of observations.

Caoutchol			"Oxide" fraction of Bloomfield and Farmer		
Diffuse halo	8° 30′—10° 0′	(4)	Diffuse halo	8° 30′—9° 48′	(3)
Ring 1	10° 46′	(4)	Ring 1	10° 41′	(3)
Ring 2	12° 3′	(4)	Ring 2	11° 58′	(2)
Ring 3	13° 36′	(2)			
Ring 4	17° 53′	(1)			
Ring 5	19° 4′	(2)			
Ring 6	20° 19′	(1)			
Ring 7	21° 43′	(1)			

The series of rings for caoutchol is quite distinct from that of frozen raw rubber, and indicates a higher degree of regularity than is possessed by amorphous rubber. The precise nature of this structural regularity is not at present known. The rings are completely absent from the photographs of all artificially oxidized rubbers so far examined, but a halo and two rings have been observed in x-ray photographs of the "oxide" fraction separable from natural rubber by the technique of Bloomfield and Farmer.[6] Data for the latter are included in the table above, from which it is seen that the photographs resemble those of caoutchol in the size of the halo and the position of the rings. They were however, much less distinct and showed more general diffused scattering. The "oxide" fraction, unlike caoutchol, is an inelastic gum. Roberts[10] has reported the existence of sharp rings in the x-ray diffraction pattern of unstretched caoutchol. Her unpublished data have been examined by G. A. Jeffrey, who states that they are not significantly different from his own, and that he therefore cannot support the suggestions made by her in the publication above referred to.

A sample of caoutchene received from Malaya was found by G. Gee to have a molecular weight of approximately 140,000. G. A. Jeffrey found that this sample gave x-ray data identical with those given by rubber, *i.e.*, the same amorphous pattern when unstretched, the same fibre diagram on stretching, and the same crystalline powder ring pattern when frozen. No systematic study of its mechanical behavior has been undertaken, but its relatively poor elastic properties and its molecular weight, combined with the x-ray data, indicate clearly that it is merely a degraded rubber.

The above conclusions are based on evidence obtained from specimens of caoutchol and caoutchene sent to this country from Malaya. It should be stated

that it was found necessary to work with such samples because it has proved impossible to prepare in England substances having all the properties of those prepared in the East.

ACKNOWLEDGMENT

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THE STRUCTURE OF POLYCHLOROPRENE *

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INTRODUCTION

In the last few years much attention has been given to the production of highly polymerized substances for use as plastics or rubber substitutes. A large-scale attempt to manufacture synthetic rubberlike materials was made in Germany in 1914-1918, owing to a serious shortage of the natural product. The synthetic product, known as methyl rubber, was a polymer of dimethylbutadiene; it was very inferior to ordinary rubber. Since then a number of these polymers have been developed. The most notable are the Buna rubbers of I.G. Farbenindustrie (straight-chain polymers of butadiene and interpolymers with butadiene), several Russian butadiene polymers known as Sovprene, and polychloroprene (Neoprene), developed commercially on account of its superiority over natural rubber for many purposes. The chief disadvantage of most of these materials is their high cost. Many such rubberlike materials have been made from hydrocarbons with a butadiene nucleus, but only in the case of halogen substituted butadienes have the results been completely satisfactory. The most important example is the polymer of 2-chlorobutadiene or chloroprene.

PROPERTIES OF CHLOROPRENE AND POLYCHLOROPRENE

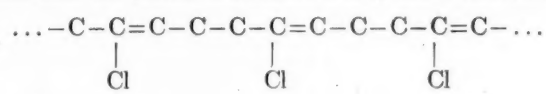
Chloroprene is a colorless liquid boiling at 59.4° C, and of density 0.9583 g. per cc. Its chemical formula is:

$$CH^2=CCl-CH=CH_2.$$

The exact molecular structure is not known, although an attempt has been made to investigate it by the application of x-ray methods at low temperatures, so far without success[1]. It is hoped to continue this work on the monomer in the solid state.

Chloroprene on polymerization may form a number of substances with widely differing properties. The principal four polymers are designated α, β, μ, and ω. The β-polymer is an oily dimer, and ω is a granular substance. The α-polymer, which is formed by spontaneous polymerization at normal temperatures (the formation is accelerated by the action of light) corresponds to milled natural rubber. μ-Polychloroprene corresponds to vulcanized rubber, and is produced by continuing the reaction which gives the α form. The conversion from the α to the μ form may be carried out by heating the material at 130° C for about 5 minutes.

Carothers, Williams, Collins and Kirby[2] suggested that, in the α-polymer, the chloroprene molecules are joined to produce a long-chain structure:



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If the polymer is heated, cross-linkages between the long chains make their appearance, giving:

$$\begin{array}{c} \ldots-A-A-A-A-A-A-A-A-A-A\ldots \\ \quad\quad\quad\

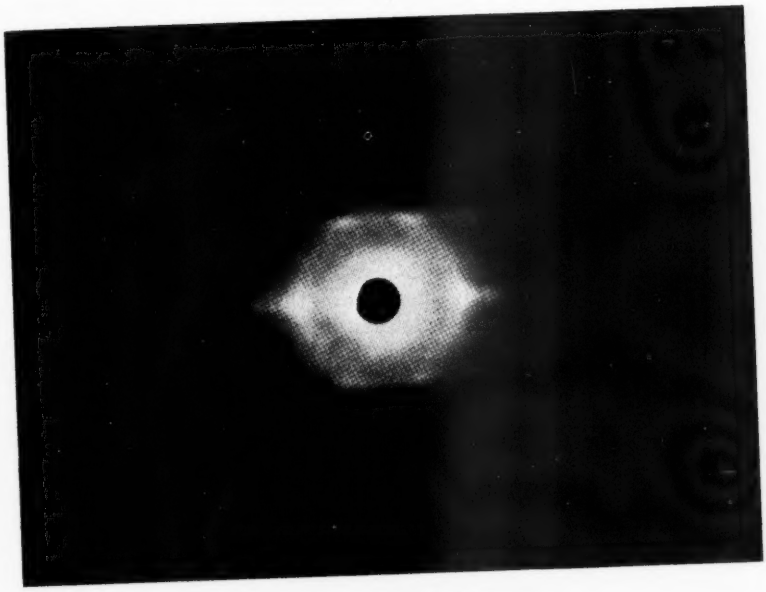
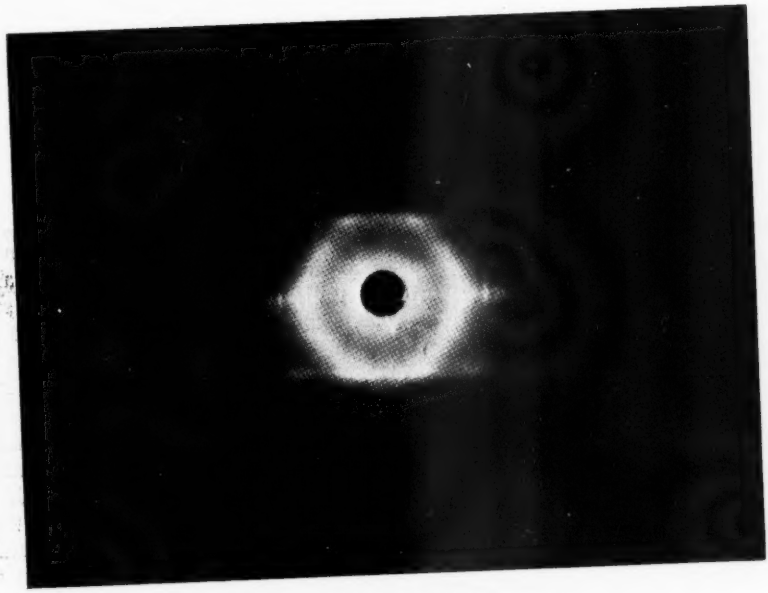


FIG. 1A.—Untreated polychloroprene.



F.G. 1B.—Light-treated polychloroprene.

clearly one of the axes of the unit cell of crystalline polychloroprene. It is found to be 4.70 ± 0.03 A.U., the mean of a number of measurements on several photographs. This is slightly lower than the value 4.8 A.U., quoted by some other authors[4]. No particulars of their experiments are given.

The first two equatorial lines are due to reflexion of Cu $K\beta$ and $K\alpha$ from the same set of planes, assumed to be the second-order reflexions from the (100) planes. The next reflexion on the equator is also fairly intense, and probably corresponds to the (001) planes, possibly the second or third order. The various possibilities will be discussed later.

Photographs were also taken with specimens of the light-treated polychloroprene in the stretched state. One of these diagrams is reproduced for comparison (Figure 1*b*, plate 1). Measurement shows that the spacings calculated from the layer line separation and the equatorial lines are identical with those for the untreated material. There are, however, two differences between the two photographs: (1) the equatorial interferences are sharper on the photograph of the treated material, and (2) there is evidence of complete Debye-Scherrer rings, their intensity being much sharper where they cut the equator.

DISCUSSION OF THE STRUCTURE OF POLYCHLOROPRENE

It is evident at once from the x-ray photographs and the measurements that there is no difference in the crystalline fine structure of the two specimens; further, it is obvious that in both cases there is an orientation of the long chains, so that most of them lie parallel to the fibre axis, caused by stretching. In the previous section, it was mentioned that the treated material was insoluble in toluene, and also that it showed increased toughness. Both these facts suggest cross-linking of the long chains induced in the substance by illumination. It is estimated that, with an average chain length of 300 units, a 1 per cent degree of cross-linking would be sufficient to produce insolubility.[3] This is supported by the x-ray results; the increased sharpness of the equatorial interferences after illumination of the specimen may well be due to cross-linking. The same phenomenon is observed when natural rubber is vulcanized. It is thought that, during vulcanization, sulfur bridges are formed within a given chain and linkages from one chain to another.

The complete Debye-Scherrer rings, with the much greater intensity on the equatorial axis, indicate that there is a marked orientation of the crystalline regions, so that the polymerized chains lie parallel to the fibre axis, but that some of the crystalline regions are orientated at random. It is possible that the diffuseness of the layer lines with both specimens is due to a slight variation in the periodicity along the fibre axis. Katz[5] has also reported a fuzziness of the layer lines.

The theory of the crystallite or micellar structure of high polymers, and in particular rubber, has been discussed elsewhere[6], so it will not be considered now except to see how far it may be applied to the present problem. In ordinary rubber there is no evidence of cross-linking to form a net structure, so that there is practically complete ordering of the crystallites on stretching; the long main-valence chains are all parallel to the stretching direction, and with untreated polychloroprene there is also fairly complete orientation. It is very probable that cross-linking in the light-treated material prevents complete ordering of the chains parallel to the fibre axis, but that short lengths of several chains may be parallel to one another and not parallel to the fibre axis. These latter would

give rise to the random orientated crystallites. The idea of cross-linking is supported also by the decreased extensibility after treatment.

Let us now consider the crystalline structure. The periodicity along the fibre direction or *b*-axis is 4.70 A.U., and assuming the first three equatorial reflexions to be (200) β, (200) α and (003), respectively, the unit cell has dimensions (in A.U.):

$$a=8.90 \qquad b=4.70 \qquad c=12.21.$$

(It is assumed $\alpha=\beta=\gamma=90°$). There is the possibility that the third line may be the second and not the third order of (001), *i.e.*, the unit cell, again assumed orthorhombic, is:

$$a=8.90 \qquad b=4.70 \qquad c=8.14.$$

The first unit cell has a volume 511 (A.U.)^3; substituting in the expression for the density:

$$\rho=1.65\ n\mathrm{M}/\mathrm{V},$$

and calculating n, the number of chloroprene units in the cell, we obtain the value $n=3.80$. (The experimentally determined density is 1.086 g. per cc., and the molecular weight, M, of the chloroprene unit is 88.5.) n must, however, be a whole number; obviously, $n=4$, giving a calculated density 1.14 g. per cc. Taking the second set of cell dimensions and four molecules per unit cell, the density is 1.72 g. per cc. It is reasonable to suppose that the density will be slightly greater when the specimen is stretched, but the density calculated from the second set of cell data is much higher than can be accounted for by stretching. (The density of natural rubber is 0.906 g. per cc., and 0.956 g. per cc. when stretched.) It would be necessary to assume three chloroprene units in the cell, and this is incompatible with orthorhombic symmetry. An orthorhombic cell:

$$a=9.0 \qquad b=4.79 \qquad c=8.23$$

has been suggested by Krylov[7] from electron diffraction measurements. His results are reported briefly by Fuller[8], but the number of units in the cell and the density are not mentioned. It appears that the measured density and this smaller cell cannot be reconciled. It may therefore be supposed that the first cell given is probably the more correct, although this can be no more than a rough approximation to the true one. There are four chloroprene groups associated with polychloroprene chains passing through the unit cell and lying, on the whole, parallel to the *b*-axis. From the repeat distance, 4.70 A.U., it is evident that the chains are in the *trans* form. Even on this assumption there must be some modification of either the bond angles or bond lengths from the usual values, or it must be assumed that the molecule is not planar. A similar difficulty was found in fitting the isoprene groups into the rubber unit cell.

Part of a planar chloroprene chain is illustrated in Figure 2. The single-bond distance is taken as 1.5 A.U., the double-bond distance as 1.2 A.U., and the bond angles are 109° and 120°. The radius of the chlorine atom is 1.8 A.U. The repeat distance is 4.9 A.U. A possible nonplanar molecule is shown in Figure 3. This has a repeat distance of 4.7 A.U., in accordance with the x-ray data. The hydrogen atoms are not represented in these figures.

From the dimensions of the molecule and of the unit cell, it is obvious that the chloroprene groups must be packed closely together, possibly with intermolecular distances less than those usually expected.

In an endeavor to index the other equatorial reflexions, it was soon realized

that this would not be possible if all sets of indices having $k \neq 0$ were excluded. This is not unreasonable because evidently we are not dealing with a single crystal rotation type of diagram produced by rubber, but with a Debye-Scherrer

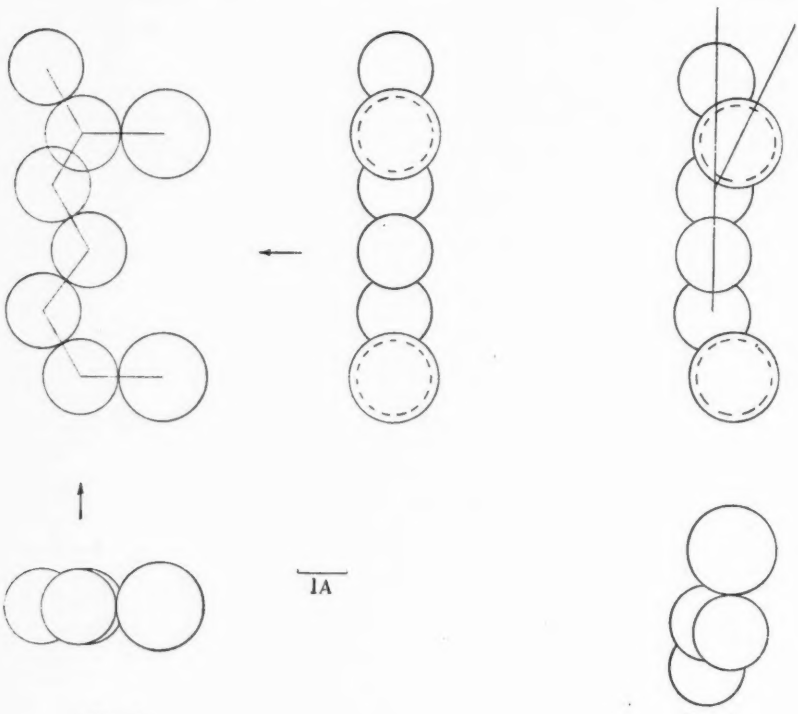


FIG. 2

FIG. 3

TABLE I

CAMERA RADIUS 3 CM. COPPER $K\alpha\beta$ RADIATIONS

Number of line	$\sin^2\theta$	d in A. U.	hkl	Intensity
1	0.20682	1.69	323	*w*
2	0.18243	1.80	413	*ww*
3	0.17000	1.87	024	*w*
4	0.12093	2.22	400	*w*
5	0.09635	2.48	311	*w*
6	0.08927	2.58	—	*ww*
7	0.08114	2.71	—	*mw*
8	0.06115	3.12	211	*ms*
9	0.05266	3.36	204	*s*
10	0.03587	4.07	003	*s*
11	0.03016	4.45	200α	*ss*
12	0.02455	4.45	200β	*s*

photograph which shows preferred orientation. The measured spacings and their corresponding indices and visually estimated intensities are given in Table I. The indexing can have no great significance, there being far too few spacings either to confirm or refute the correctness of the cell chosen.

CONCLUSION

Specimens of polychloroprene and light-treated polychloroprene have been examined by x-ray methods. There is evidently no change in the crystalline structure of the two substances, although there are differences in physical properties which are ascribed to cross-linking of the long polychloroprene chains. This conclusion is confirmed by the x-ray work. The unit cell of polychloroprene is probably orthorhombic, with dimensions $a=8.90$ A.U., $b=4.70$ A.U., $c=12.21$ A.U. From the experimentally determined density of 1.086 g. per cc., it is deduced that there are four chloroprene units in the cell. The x-ray density (for the stretched material) is 1.14 g. per cc. The long chains lie parallel to the b-axis (the direction of stretching), and four of these chains pass through the unit cell. It is concluded, from the identity period, that the chain is not planar and a possible spatial configuration is given.

ACKNOWLEDGMENT

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PHYSICAL-CHEMICAL INVESTIGATIONS OF ARTIFICIAL RUBBER

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III. A DISCUSSION OF THERMAL MEASUREMENTS *

Among the physical methods of which use has been made to explain the structure of organic compounds, thermal measurements, particularly measurements of heats of combustion, have played a particularly important part. With the aid of data on heats of combustion, it is possible to draw conclusions on the energy relations within molecules and on the heat tones of chemical transformations. Such measurements have been carried out on highly polymeric substances[1]. In some cases, the object was to study the reactions of formation. *e.g.*, polymerization; in other cases it was to explain the transformations which high polymers themselves undergo. Studies of polymerization reactions by thermal methods have shown that, in distinction to monomers, a decrease in the heat of combustion with increase in the degree of polymerization is to be expected. The polymerization process is accordingly exothermic, and the difference between the heats of combustion represents the heat of polymerization which is liberated. A direct comparison of heats of polymerization found experimentally by different investigators is, however, not possible because, in most cases, no information on the degree of polymerization, branching of the chain molecules, or other significant properties of the polymers are given.

Measurements have shown that the heat of combustion of Buna-S is lower than that of monomeric butadiene. It is more accurate to calculate the heat of combustion of Bune-S, not on the molecular weight of butadiene (54), but rather on a mean molecular weight of 64.1, which represents the value obtained if the ratio of styrene to butadiene is assumed to be 20:80.

Flory[2] has calculated the heats of polymerization of a series of vinyl compounds. The value for butadiene is 20 large calories per mol. The heats of polymerization of Buna-S and also of Buna-85 are approximately twice this value, as was to be expected from earlier measurements. The reason for this unexpectedly great difference cannot be explained by any experimental data available at the present time. Possibly the development of a relatively high network structure in the Buna molecule play so great a part that this alone accounts for the difference in the heats of polymerization. Hock and Leber have shown[3] that completely formed high polymerys can undergo further polymerization. When a solution of rubber or of Buna-85 is exposed to the influence of silent electric discharges, the viscosity of the solution increases with increase in the time of treatment, until, ultimately, gelling takes place. Under the influence of such electric treatment, raw rubber takes on more and more the character of vulcanized rubber. Here too, the heats of combustion of electrically treated samples decrease with increase in the time of treatment, until surprisingly low values are reached when the rubber has become insoluble and "vulcanized." Accordingly the formation of the network which characterizes this pseudovulcanization is accomapnied by a large decrease in energy.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 17, No. 3, pages 33-36, March 1941.

Table I gives some typical measurements and heats of polymerization which have been calculated from these measurements.

The investigation of Roth, Wirths and Berendt[1] were carried out with the primary purpose of explaining the process of thermal softening of Buna-S, and the resultant hardening reaction, from the point of view of thermochemistry. The data assembled in Table II show a clearly defined decrease in the heat of combustion with increase in the degree of degradation.

Under certain other conditions also, thermally degraded Buna-S shows heats of combustion which fall within the same order of magnitude. Only samples with hardnesses of 400 to 500 (Defo) fail completely to come within these limits and, instead, show much higher values than would be expected. When Buna-S which has been degraded is kept in storage, it undergoes slow, progressive changes which are manifest in a decrease in plasticity and an increase in its elastic component. It is possible that this hardening which takes place during storage is responsible for its anomalous behavior.

It is interesting that, in spite of the decrease in size of the molecule, which unquestionably takes place when Buna is degraded, there should be a decrease in the heat of combustion. Actually, the degradation of Buna is an exothermic process which involves attack by oxygen on the Buna. But although the decrease in heat of combustion can perhaps be satisfactorily explained in a qualitative way by assuming that oxidation takes place, it cannot be attributed solely to any such oxidation. For the transformation of a $-CH=$ group into a $-CO-$ group, the loss of energy is, according to Roth, Wirths and Berendt[1], 58 large calories. In the case of Buna-S, the greatest difference in the heats of combustion is approximately 24 large calories (based on a molecule with weight of 64.1), so one oxygen atom should react with approximately three butadiene molecules. By weight this is approximately 10 per cent of oxygen, based on the Buna-S. But all experiments have led to a contrary result; in fact, up to the present time, no weighable quantity of oxygen has ever been found to be taken up by Buna in any normal degradation process. If oxidative degradation is carried out under conditions such that one molecule of oxygen attaches itself to a double bond by a peroxidic reaction, so that cleavage takes place at this point, and if it is further assumed that, when a state of extreme degradation is reached, the molecular weight decreases to 20,000, the oxygen consumed is 0.16 per cent, which corresponds to a ratio of oxygen to Buna of 32 to 20,000.

Unfortunately, data on the molecular weight and oxygen consumption of Buna are not available; nevertheless, based on general knowledge, the assumptions above seem to be correct, at least in their order of magnitude. In any event, the consumption of oxygen is extraordinarily small, and the fear that under some conditions too little air might be present in a kettle used in making Buna[7] is, from the stoichiometric viewpoint, certainly quite unfounded. The increased air pressure which is in most cases employed in degrading Buna technically has a direct accelerating action on the process, since the rate of softening depends on the pressure[8].

In contrast to the behavior of Buna-S, it has been shown by Wolshinski and Loginowa[9] that sodium-butadiene rubber (SKB) does not absorb an appreciable quantity of oxygen, either at 20° C or at 100° C, and that its properties do not change. However, manganese oleate and copper oleate act as catalysts of oxygen absorption, and hard, pulverulent products containing 10-15 per cent of oxygen, supposedly in the form of carbonyl groups, are formed.

It is interesting to compare the heats of combustion and the mechanical

TABLE I

HEATS OF POLYMERIZATION OF VARIOUS COMPOUNDS

Monomer	Polymer	Heat of combustion (calories per gram)		Difference		Author
		Monomer	Polymer	Calories per gram	Large calories per base mol	
Styrene	Polystyrene	10,046	9,914	132	13.7	Luschinsky[4]
Isoprene	Natural rubber	11,097	10,820	277	18.8	Jessup[5]
Butadiene	Buna-85	11,300	10,615	685	37.0	Hock and Leber[3]
Butadiene + styrene (80:20)	Buna-S	11,050 (calculated)	10,396	654	41.9	Roth, Wirths and Berendt[6]
Natural rubber	Electrically treated	10,710	10,395	315	21.4	Hock and Leber[3]
Buna-85	Electrically treated	10,615	10,440	175	9.4	Hock and Leber[3]

properties of the vulcanized material. By thermal softening, the technically important properties of Buna in the vulcanized state are impaired considerably. Figure 1 shows the characteristic way in which the tensile strength and elasticity depend on the hardness, *i.e.*, on the extent of degradation. Whereas the tensile strength increases as an almost straight-line function of the hardness, the rebound

TABLE II

HEATS OF COMBUSTION OF BUNA-S DEGRADED TO VARIOUS DEGREES

Treatment	Hardness (Defo)	Heat of combustion (calories per gram)	Difference	
			Calories per gram	Large calories per base mol
None	5000	10,396	...	...
15 min. at 130° C.	3250	10,367	2.9	1.9
30 min. at 130° C.	1650	10,290	106	6.8
60 min. at 130° C.	950	10,249	147	9.4
100 min. at 130° C.	700	10,021	375	24.0

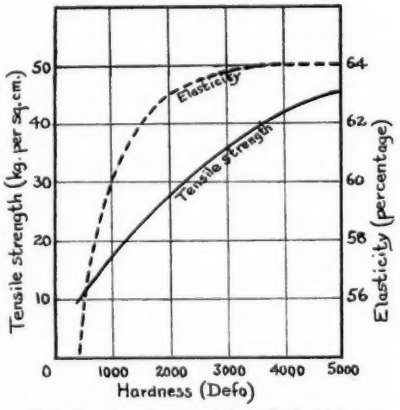

FIG. 1.—Tensile strength and elasticity as functions of the degradation of an unloaded Buna-S mixture.

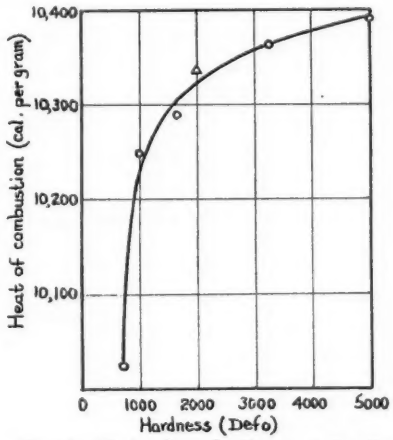

FIG. 2.—Heats of combustion as a function of the degradation of Buna-S.

elasticity of untreated Buna with a Defo hardness of 5000 remains unchanged to a hardness about 2000; below this range the elasticity decreases at first slowly, and then, below a hardness of 1000, rapidly.

If the heats of combustion are ploted as a function of the Defo hardness values, as in Figure 2, the curve obtained resembles in its general character that which relates elasticity and hardness (see Figure 1). If this resemblance is not accidental, it is probably an indication that elasticity and heat of combustion are influenced fundamentally by the same reactions. Attention is called to this new relation, without going further into any theoretical discussion.

Other degradation processes have been studied with respect to their effects on the heats of combustion of high polymers. Messenger[10] determined the heats of combustion of natural rubber which had been masticated to various degrees, but could find no change in this property by mastication. These measurements were, of course, made a long time ago, so it is possible that differences which actually did exist could not be detected by the relatively inexact methods used

at that time. Since it may be assumed that the extraordinarily precise method developed by Roth makes it possible to detect very small differences in heats of combustion, experiments were carried out with masticated rubber. Probably it will be possible from these measurements to draw conclusions as to the changes in chemical combination which takes place during mastication.

Fortunately specific heats were also measured and published in the preceding work. This property is above all a measure of the capacity for storing energy, *i.e.*, of the degree of freedom-of-movement of the molecules. In the case of high polymers, this means that rigid molecules, which have a highly developed network structure and are therefore immobile, have smaller specific heats than mobile fibre molecules. A restriction of this free mobility can be brought about by the formation of a network structure and by other influences, *e.g.*, steric hindrance.

The specific heats of a few highly polymeric substances are recorded in Table III. The values show that Buna-S and natural rubber have approximately

TABLE III

SPECIFIC HEATS OF A FEW HIGH POLYMERS

Product	Specific heat (calories per gram per degree)	Author
Buna-S, untreated	0.472	Roth, Wirths and Berendt[6]
Buna-S, 400-500 Defo hardness	0.465	Roth, Wirths and Berendt[6]
Buna-S, hardened again	0.459	Roth, Wirths and Berendt[6]
Natural rubber	0.449	Bekkedahl and Matheson[11]
Natural rubber, vulcanized with 2% sulfur	0.510	McPherson and Bekkedahl[12]
Natural rubber, vulcanized with 32% sulfur	0.341	McPherson and Bekkedahl[12]
Cellulose	0.364	
Phenolic resin	0.35	Vieweg and Gottwald[13]
Polystyrene	0.30	Vieweg and Gottwald[13]

the same specific heats. Furthermore, during the degradation process, these values remain almost unchanged, and likewise are changed only slightly by the accompanying hardening reaction. From this it may be concluded that degradation brings about no change in the mobility of the Buna molecules themselves. Even the slight degree of network formation during the hardening reaction is apparently without influence on this socalled micro-Brownian movement.

An analogous case is found when the freezing points are determined[14], for freezing points likewise are governed primarily by intramolecular movements of the molecules. When determined by the dilatometric method, the freezing points remain constant throughout the range of degradation, including the hardening stage. The development of a network structure, which takes place during the hardening process, stops only the macro-Brownian movement, *i.e.*, plastic flow, and does not change the intramolecular movement. A similar case is to be found with natural rubber and its low-sulfur vulcanizates. The network which is developed by the combination of a small percentage of sulfur affects only the macro-Brownian movement and, consequently is without any great influence on the specific heat and on the freezing range[15]. Only the higher proportions of combined sulfur is the movement of the chain itself inhibited, and this immobility becomes manifest in a rise in the freezing temperature and in a decrease in the specific heat.

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[12] McPherson and Bekkedahl, *J. Research Natl. Bur. Standards* **14**, 601 (1935). The great decrease from 0.510 to 0.341 is in part explainable by the sulfur which has combined, for sulfur has a much lower specific heat.
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RUBBER IN VIBRATION *

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INTRODUCTION

In most of the uses to which rubber is put, it is subjected to deformations which are relatively small compared to the ultimate deformation of which the rubber is capable. For many products, such as vehicle tires, motor mountings, and belts, the deformations are periodic. There is, therefore, a great deal of interest attached to the physical properties of rubber when measured under vibratory, as contrasted to static, conditions.

The use of rubber in mountings for the absorption or isolation of vibration, with which this paper is principally concerned, has led to a number of systematic investigations of its static properties from the standpoint of the engineer who might be interested in employing it for such purposes. As representative of such contributions may be cited the work of Keys[1], Smith[2], Brown[3], Haushalter[4], Hirshfeld and Piron[5], and Kimmich[6]. The principal concern was to determine the rules which govern the deformation of rubber pieces of various sizes, shapes and hardnesses. Related questions of permanent set, creep, and the effect of temperature also came into the discussion. The importance of dynamic measurements was realized, but information on this phase of the subject was beyond the scope of the work.

Published investigations of the vibration properties of rubber, with a few exceptions, have not had much direct connection with the design of mountings. Usually they have been carried out on relatively small, standardized test-pieces, the principal interest being the comparison of the properties of different rubber compositions for the purpose of developing compounds with improved dynamic properties. In some cases the work has been of a fundamental research character on the nature of rubber elasticity. The following references, if consulted, will give a fairly comprehensive picture of what has been done, although they are by no means a complete bibliography. Vogt[7] has reviewed the work of Bouasse, Wiegand, Gerke, Meyer and Ferri, and others dealing with cyclic extensions and contractions of stretched rubber. Kosten has discussed the general character of the dynamic results which have been observed when rubber is subjected to periodic vibrations, and has extended the data by his own investigations[8]. Roelig[9] has reported extensive results on dynamic tests carried out with forced vibrations. Naunton and Waring[10] used electrical methods for driving the rubber sample and measuring the dynamic properties. Yerzley[11] employed a system where free oscillations occurred. Gehman, Woodford, and Stambaugh[13] studied the effect of pigment loadings on the vibration properties.

Rubber mountings are now generally made with the rubber moulded and adhered to metal during vulcanization. The rubber may act in compression, tension, shear, or torsion. Frequently there are complicated combinations of such superposed stresses in a mounting. The mountings which have been designed and developed for specific purposes show an almost infinite variety in geometrical design, size, shape, and type of action.

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The work reported here describes equipment which is useful for observing and studying such mountings under vibration, and gives some of the more general results of such studies.

DESCRIPTION OF APPARATUS AND PROCEDURES

The principles of the machine used for exciting the vibrations are evident from the diagram of Figure 1. The central carriage, held in place by centering springs of negligible stiffness, is set into vertical vibration by the opposite rotation of two geared shafts carrying eccentric weights at each end, a well-known device. The centering system consists of thin horizontal cantilever blades, one of which is attached at each corner of the carriage as indicated in Figures 1 and 2. The shafts are driven by a horizontal belt from a variable speed d.c. motor. The amplitude of vibration reaches large values only in the neighborhood of the resonance frequency, which is determined by the stiffness of the

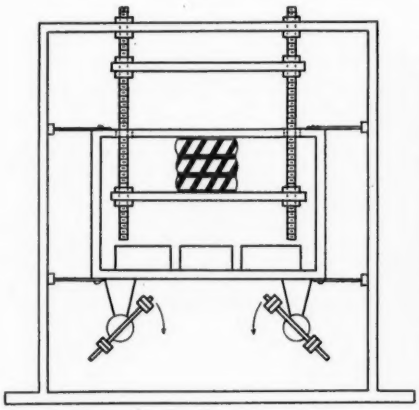

FIG. 1.—Diagram of machine.

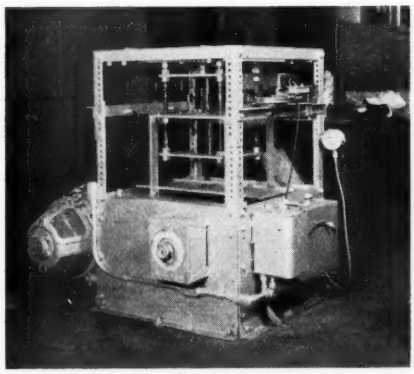

FIG. 2.—Photograph of machine.

rubber mountings and the mass of the vibrating carriage. From the resonance frequency, the dynamic stiffness can be calculated, and from the amplitude of vibration at resonance a value of the damping can be computed.

A photograph of the machine is shown in Figure 2. The platens on which the test-pieces are mounted are fourteen inches square and capable of a separation of about eight inches, so, with suitable fittings, all types of rubber mountings of ordinary size can be accommodated. This includes mountings for which the rubber vibrates in tension, compression, shear, or torsion under various superposed static stresses. In the photograph, the test-pieces are mounted for vibration in shear. In this arrangement, the test-pieces under the platen are subjected to a greater static load than those above, because of the weight of the carriage. When the weight of the carriage is small compared to the total static load, this inequality of static load is not objectionable. In many cases, however, it is preferable and simpler not to have the double test-piece, but to use the weight of the carriage to impress the static load on a test-piece under the platen. The weight of the carriage is normally 174 pounds, but it can be readily varied in the range from 140 to 400 pounds by the removal or addition of weights. There is usually little difficulty in arranging things to secure resonance at a

speed of about 600 r.p.m. If a particular rubber mounting is too stiff, it is often possible to use two or more of the units in series; if it is too soft, several can be used in parallel. Thus it has been found as a rule to be even simpler to adjust the stiffness than it is to adjust the weight of the carriage. This restriction to approximately the same frequency assists in the comparison of results, and insures operation of the machine at a speed such that reactions through the frame are completely negligible.

Figure 3 is a photograph of the recorder used for registering the vibrations. It was constructed with the aid of parts from a moving picture projector. Standard 16-mm. film is moved around a horizontal drum at a constant speed by a synchronous motor. Exposed film is used, from which the gelatin has been removed by soaking in warm, dilute hydrochloric acid. The film is scratched by a stylus attached to the vibrating carriage. Sample records are reproduced

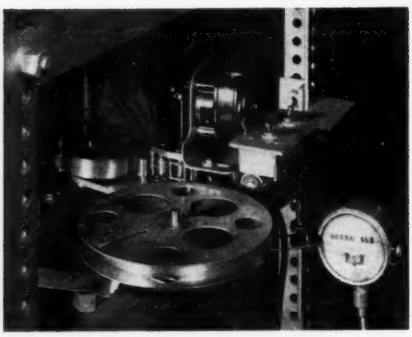

FIG. 3.—Photograph of recorder used for registering vibrations.

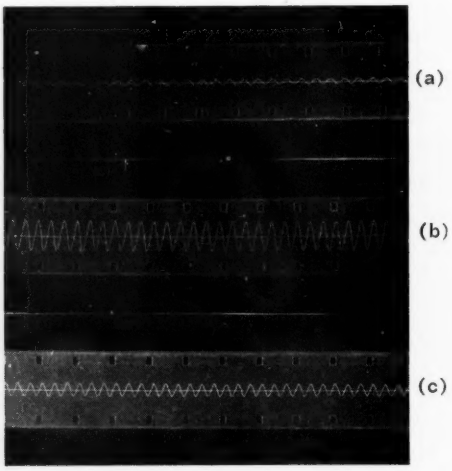

FIG. 4.—Reproduction of portions of typical record (torsional vibrations). (a) Speed below resonance; (b) resonance; (c) speed above resonance.

in Figure 4. The procedure for securing records was as follows: The speed controlling rheostats were left at one setting until the speedometer (shown at the right in Figure 3) indicated that a constant speed had been attained. The recorder was then started and six or eight inches of record secured. The recorder was stopped and the speed of the machine changed by an amount shown by the speedometer and a short record at this speed secured. In this way, step by step, the resonance peak was passed through. The time required to secure a record is about five minutes.

The amplitudes are measured by projecting the record on graph paper, using the optical system of a microphotometer which was available. The magnification can be checked by measuring the notches in the film. The frequency corresponding to a given amplitude is determined by measuring the length of ten waves, making use of the micrometer screw which moves the platform of the microphotometer. Considerable time is required to measure a complete record. Usually it is sufficient to measure four or five points near the resonance peak. For this, ten or fifteen minutes are ample.

After the record is measured, a few simple calculations are necessary. There are four rotors, each carrying two equal masses w at radii r_1 and r_2 from the center. The driving force for the vibration is, therefore, the centrifugal force:

$$F=(16\pi^2/32.2)w(r_1-r_2)(\text{r.p.m.})^2/3600 \quad (1)$$
$$w=0.441 \text{ lb.}$$

The units for r_1 and r_2 are feet and for F, pounds.

Each mass w consists of two nuts screwed against each other on a threaded rotor. It is frequently desirable to change the value of the driving force. This is done by always keeping r_1 fixed and changing r_2 on each rotor by bringing the nuts up against spacer blocks which locate the nuts accurately with reference to the axles. The spacers, of course, are then removed. To determine the position of the weights for dynamic balance of the machine, resonance amplitudes, for a given mounting, were plotted against the values of (r_1-r_2) as determined by the spacer blocks. This plot is shown in Figure 5. The intercept of the straight line with the axis gives the point of dynamic balance. By use

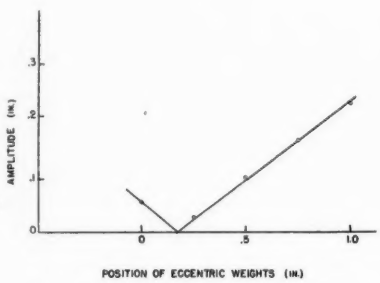

FIG. 5.—Dynamic balance of machine.

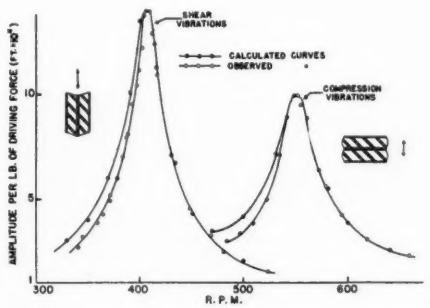

FIG. 6.—Comparison of observed and calculated resonance curves.

of Equation (1), a chart was then plotted, each curve of which gave F as a function of the r.p.m. for one of the spacer blocks. Thus the value of the driving force at a given r.p.m. can be read from the chart. Since the r.p.m. is proportional to the reciprocal of the wave-length which is measured on the record, it is also convenient to read the r.p.m. values from a plotted curve. In this way, corresponding values of r.p.m. driving force, and amplitude can be easily secured.

THEORY

The procedure which has been described has the effect of correcting the results to an exciting force independent of the frequency, and thus reducing the interpretation of the results to the simple one degree of freedom system, the analysis of which is given in every textbook on vibration.

The equation of motion is:

$$M\ddot{x}+\alpha x+s\dot{x}=F\cos pt \quad (2)$$

M – mass (lb./32.2);
x – displacement from equilibrium position (ft.);
α – constant of proportionality between the internal frictional resistance of the rubber and the velocity (lb./ft. per sec.);

s – stiffness of rubber (lb./ft.);
F – maximum value of sinusoidal driving force (lb.);
p – angular frequency, 2π(r.p.m.)/60.

The steady state solution of Equation (2) is:

$$x=\frac{F\cos(pt-\theta)}{[(s-mp^2)^2+\alpha^2p^2]^{\frac{1}{2}}} \tag{3}$$

$$\tan\theta=\alpha p/(s-mp^2) \tag{4}$$

The value of p for the maximum amplitude of vibration is given by:

$$p^2=s/M-\alpha^2/2M^2 \tag{5}$$

Usually the second term can be neglected so that, at resonance:

$$p_n^2=s/M \tag{6}$$

$$x_{max}=F/\alpha p_n \tag{7}$$

These equations serve to determine s, the dynamic stiffness of the rubber and α, its internal damping coefficient. It is known, however, that for most materials, including rubber, α is a function of the frequency[13]. At resonance, x/F is given by $1/\alpha p_n$ in accordance with Equation (7). Finite amplitudes at resonance are observed at all frequencies, so it can be seen in a general way that, as p increases, α diminishes and *vice versa*. As a matter of fact, the amplitude at resonance for rubber vibrations, as the mass of the system is varied and F held constant, is, to a first approximation, independent of frequency, so the product αp is very nearly constant.

This type of internal friction has been designated by Kimball[14] as solid friction. Kimball has developed the theory in terms of the stress and strain per unit volume of the vibrating medium, and has defined the quantity η, the coefficient of normal viscosity, as the constant of proportionality between the velocity damping force and the time rate of change of the strain.

The logarithmic decrement for free vibrations is shown to be:

$$\delta=\pi\eta p_n/E \tag{8}$$

where E is Young's modulus of the material.

Since observation showed δ to be independent of frequency, Kimball concluded that ηp was invariant.

Illustrating still another viewpoint, Kosten[15] has pointed out that the quantity $\alpha p_n/s$ is analogous to tan δ in alternating current theory, where δ is the angle of loss, and should not be confused with the logarithmic decrement given by Equation (8). Kosten has expressed his results for rubber in terms of this angle.

The logarithmic decrement is connected with α by the relationship:

$$\delta=\pi\alpha/(sM)^{\frac{1}{2}}=\pi\alpha/Mp_n=\pi\alpha p_n/s \tag{9}$$

It is general practice to use an approximate relation for the logarithmic decrement, *viz.:*

$$\delta=\Delta W/2W=\Delta y/y \tag{10}$$

Here W is the vibrational energy and y is the amplitude. Δ represents the change in these quantities for two successive free vibrations. $\Delta W/W$ is the damping.

In the case of rubber the damping is sometimes so large that the above approximations are inaccurate. Hence, it is preferable to define a quantity called the dynamic resilience as the percentage of the vibrational energy remaining in the second of two successive free vibrations[12]. This is given by:

$$R=100 \exp [-2\pi\alpha/Mp_n]=100 \exp [-2\pi\alpha p_n/s]=100 \exp [-2\pi p(\eta/E)] \quad (11)$$

The percentage damping is $(100-R)$.

Although it has been found expedient to work up the data in such a way as to correct for the variation of the exciting force with frequency, it is worthwhile to give some consideration to the theory underlying the actual response when, as in this case, the amplitude of the force varies with the square of the frequency.

A general analysis for such a system has been given by Bernhard.[16]

The amplitude is:

$$x=\frac{mrp^2 \cos (pt-\theta)}{[(s-Mp^2)^2+\alpha^2p^2]^{\frac{1}{2}}} \quad (12)$$

where m is eccentric rotating mass,
and r is eccentricity.

TABLE I

CHARACTERISTICS OF RESONANCE CURVES

	Constant force amplitude	Force amplitude proportional to p^2
1.	$x \rightarrow F/s$ as $p \rightarrow 0$	$x \rightarrow 0$ as $p \rightarrow 0$
2.	Maxima shift to lower frequencies as damping increases	Maxima shift to higher frequencies as damping increases
3.	$x \rightarrow 0$ as $p \rightarrow \infty$	$x \rightarrow mr/M = mrp_n^2/s$ as $p \rightarrow \infty$

The characteristics of the resonance curves from Equation (12) in comparison with those from (3) are stated in Table I.

These characteristics have been observed for resonance curves secured in this work with rubber.

When rubber mountings are used for the isolation of vibrations, the fundamental principle is that the natural period of any mode of vibration of the system should be lower than that of any impressed frequency which will excite the mode in question or any mode coupled with it.

For a system with one degree of freedom, the transmitted force is given by:

$$F_t=F\left[\frac{1+[2(\alpha/\alpha_c)\cdot(p/p_n)]^2}{(1-p^2/p_n^2)^2+[2(\alpha/\alpha_c)p/p_n]^2}\right]^{\frac{1}{2}} \quad (13)$$

where F_t is transmitted force;
α, p, and F are defined as in Equation (3);
p_n is natural frequency of system, and
α_c is critical damping $=2Mp_n$.

For zero damping:

$$F_t=\frac{F}{1-(p/p_n)^2} \quad (14)$$

The relationships involved in these formulas are analyzed by den Hartog[17], and need not be repeated here. It is sufficient to point out that, in accordance

with Equation (14), rubber mountings are carefully designed to avoid resonance conditions during operation. This does not detract from the expediency of using resonance conditions to study the vibrational properties of the mountings.

For vibration isolation, the natural frequency of the system is set below the resonance frequency. If it is set too low, the system will develop instability for static loads, transient accelerations, etc. Hence a balance must be struck in the design between vibration isolation and static stability. Usually it is desirable to provide some type of snubbing to preclude excessive transient deflections.

TEST OF VIBRATION THEORY AS APPLIED TO RUBBER VIBRATIONS

Figure 6 compares observed and calculated resonance curves for both shear vibrations and compression vibrations. Sandwiches of rubber adhered to metal were used in the test. The durometer hardness of the rubber was 30, size of the sandwiches $2''\times4''\times1''$. As ordinate is plotted the amplitude per pound of driving force and, as abscissa, the r.p.m. of the driving force. The calculated curves were obtained from Equation (3), and were fitted to coincide with the experimental curves at the resonance peak. A small systematic deviation between the calculated and observed curves occurs on the low frequency side of the resonance peak, the observed values of the amplitudes falling below the calculated ones. This is due to the fact that s in Equation (2) is not strictly a constant. The known variation of α with frequency cannot account for this deviation because, at the base of the peak, where the deviation is largest, the amplitude is practically independent of α, and is determined by the term $(s-mp^2)$ in Equation (3).

Although the deviation from the theoretical curve is rather small, it seemed worthwhile to find the cause, for what light it might throw on any peculiarity of the dynamic properties of rubber or the accuracy of the work.

A variation of s could be shown by calculating s for different points of the experimental curve using, instead of Equation (6), an equation derived from Equation (3), *viz.*:

$$s^2=\left(\frac{p_2^2}{a_1^2}-\frac{p_1^2}{a_2^2}\right)\left(\frac{1}{p_2^2-p_1^2}\right)+p_1^2p_2^2M^2 \qquad (15)$$

Here p_1 and p_2 are frequencies for two points selected for the calculation, and a_1 and a_2 are the corresponding x/F values or unit amplitudes from the curve for the two points. It was found that the value of s depended somewhat on the two points selected for the calculation. If this variation of s were due to a dependence on frequency, there should be a deviation from the theoretical curve on the high frequency as well as on the low frequency side of the resonance peak.

The remaining possibility is that s varies with the amplitude in such a way that it is larger for small amplitudes than it is for large ones. Because of the way in which the vibrations were excited, by centrifugal force, the amplitudes were larger on the high frequency side of the resonance peak than they were on the low frequency side, although the amplitudes per unit force, which are plotted in Figure 6, do not show this. This accounts for the appearance of the deviation between the observed and calculated curves on the low frequency side of the peak and not on the high frequency side.

If the centering springs of the vibrating carriage had any influence on the observed value of s, the opposite effect would be expected and s become greater as the amplitude increased.

The variation of s with amplitude can also be shown directly by securing resonance curves using different driving forces so as to obtain different amplitudes at resonance. Two such curves are shown in Figure 7. The test-pieces were two parallel rubber cylinders adhered at the ends to metal, 30-durometer hardness, height $1\frac{3}{8}$ inch, diameter 2 inches. For the lower amplitude, the resonance peak is displaced to a higher frequency relative to the peak secured at the higher amplitude. For gum stock, under ordinary circumstances, this dependence of stiffness on amplitude is negligible. When the hardness of the rubber is increased by the addition of appreciable volumes of carbon black or other pigments, the effect can become very pronounced.

Figure 8 shows the large deviation which occurs between calculated and observed resonance curves for a tire tread stock containing about 25 volumes of gas black. Here the test-piece was a rectangular block, $1'' \times 1'' \times 2''$, vibrated lengthwise in compression. The effect of the dependence of modulus on amplitude is to give a much sharper resonance peak than is predicted by the simple theory. The internal friction, determined by the quantity α in Equation (7), decreases

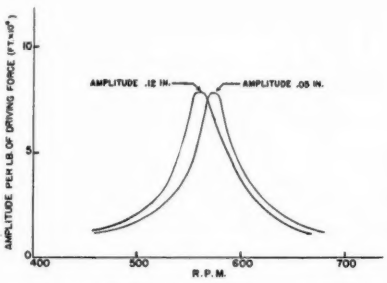

FIG. 7.—Effect of amplitude on stiffness.

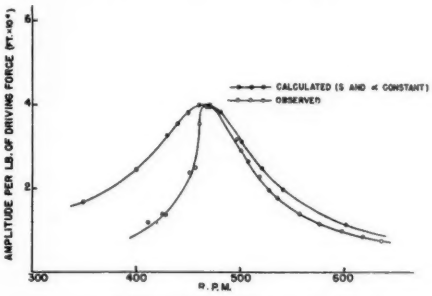

FIG. 8.—Calculated and observed resonance curves for tread stock.

with increase of amplitude in such a way that calculated values of resilience increase with increase of amplitude. Naunton and Waring[10] and Gehman, Woodford, and Stambaugh[12] also observed a dependence of modulus and resilience on amplitude for tread stocks, at much higher frequencies than those here used. Kosten[15], on the other hand, for smaller amplitudes and probably a smaller range of amplitudes, reported that both the angle of loss and the stiffness were independent of amplitude.

The reason for the dependence of the stiffness on the amplitude is somewhat obscure. Heat generation in the test-piece is proportional to the square of the amplitude of vibration. On this account temperature changes would be in the proper direction to account for the results. One of the reasons for not dismissing the dependence of s and R on the amplitude as being entirely due to the temperature rise is that the temperature rise in these experiments was so small. For the test-piece for which the curve of Figure 8 was secured, the temperature rise, measured by a needle thermocouple inserted into the test-piece, did not exceed 5°C. Another reason is that the observed values of s are independent of frequency. A heating effect should also occur for frequency variation. Results of Weber and Goeder[18] give some indication that an increase in modulus for small stresses may be a very general property of materials.

The dynamic modulus of rubber is generally observed to be somewhat higher than the static modulus. Also, the dynamic modulus is independent of the

frequency. The question now arises as to how low the frequency would have to be for the dynamic modulus to decrease and approach the static value. This is somewhat of a dilemma, since the greater dynamic values are observed at the lowest frequencies which could be reached in this work, *viz.*, 250 to 300 cycles per minute. If there were a true dependence of the dynamic modulus on amplitude, *i.e.*, not caused by temperature rise, it could be said that the dynamic modulus approaches the static modulus as the amplitude increases, regardless of the frequency. For this reason, the dependence of dynamic modulus on amplitude is of some theoretical interest. The points raised here require further carefully designed and controlled experiments for full understanding. The deviation of the dynamic from the static stiffness for rubber has never been satisfactorily explained. The most probable basis for an explanation appears to lie in the elastic imperfections of rubber described by such words as hysteresis, creep, relaxation, set, "memory", etc. It is possible that a mathematical formulation of rubber vibrations in terms of the relaxation theory of Maxwell or the "memory" theory of Boltzmann would account for these dynamic effects. The decrease of s with amplitude is a favorable factor in the performance of rubber mountings for the isolation of vibration, as it tends to shift the natural frequency to lower values as vibration amplitude builds up. But the effect is a small one.

PROPERTIES OF RUBBER VIBRATING IN COMPRESSION

Rubber shows peculiar characteristics when placed under compressive stress. When equal uniform stresses are applied to two opposed parallel faces of a block of rubber, instead of compressing in the ordinary sense, the rubber undergoes a deformation without appreciable change in volume. The rubber bulges out at the sides and a complicated, nonuniform stress distribution is set up in the rubber. The stiffness depends not only on the modulus of the rubber but on the shape of the piece and on the friction between the rubber and the end plates. The static effects have been thoroughly studied[6].

For test-pieces similar in shape but varying in size, a given stress produces the same percentage compression. For pieces with different shapes, the stress required to do this depends on the ratio of the area of the loaded surface to the area of the free surfaces, but otherwise is practically independent of the shape. When the stress required for a constant percent compression is plotted against the shape factor, load area/free area, a smooth curve is obtained. A family of such curves for rubber compositions of different hardnesses gives the empirical information required for the static design of rubber compression mountings.

In contrast to the results for rough end-plates or for test-pieces in which the rubber is adhered to the end-plates, are those for lubricated end-plates. In this case, as compressive stress is applied, the sides of the rubber remain straight, a uniform condition of stress exists throughout the rubber, and a value for a compression modulus characteristic of the rubber composition can be obtained. Even so, the calculated modulus is constant only if the calculation is based on the actual cross-section, which increases with the stress. Figure 9 illustrates, for a cylindrical test-piece, the effect which is being discussed.

For the case of no slipping at the end-plates and low shape-factors, the calculated modulus approaches the value secured with lubricated end-plates. This is the lowest value. For relatively high shape-factors, such as 2.5, no slipping, the calculated modulus may exceed, by a factor of ten or more, the modulus for lubricated end-plates.

The fundamental principle which has come out of the static tests is that rubber test-pieces, similar in shape but varying in size, subjected to the same compressive stress, undergo the same percentage deformation. It might be taken for granted that this same rule applies to the dynamic stiffness, especially since some evidence to this effect already exists[15]. Nevertheless, it seemed worthwhile to make a carefully controlled experiment to test the applicability of this principle under dynamic conditions.

In carrying out the experiment, it was desirable that test-pieces of identical composition and cure, of the same shape but of different size, be subjected to the same percentage static compression, set into vibration with the same resonance frequency and the same percentage amplitude. The test-pieces were cut from

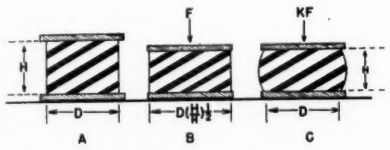

FIG. 9.—Rubber in compression. (A) original cylinder; (B) lubricated end-plates; (C) no sliding at end-plates.

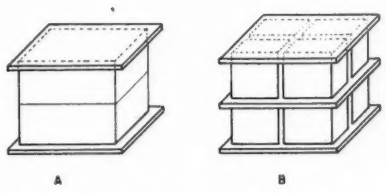

FIG. 10.—Arrangement of test-pieces for test of principle of dynamic similarity.

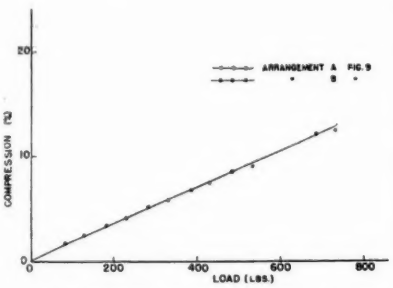

FIG. 11.—Static results of similarity test.

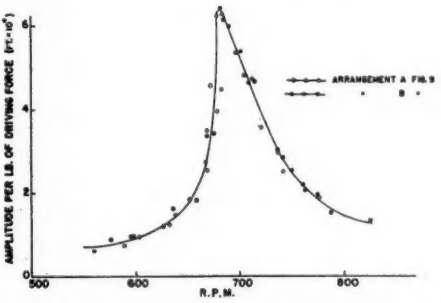

FIG. 12.—Dynamic results of similarity test.

a slab of rubber, thickness 1.25 inches. The durometer hardness of the rubber was 40. Two squares were cut, three inches on a side. These were cemented together to give a rectangular block $3\times3\times2.5$ inches. Eight small blocks were cut from the slab, with dimensions $1.5\times1.5\times1.25$ inches. The eight small pieces, when mounted as shown in Figure 10, should have, according to the above principle, the same stiffness as the single large block. All of the end surfaces of the blocks were loaded against fine sandpaper to avoid slipping at the ends. The static stiffnesses of the single large block and the eight small blocks were found, in fact, to be identical. The results of this Olsen machine test are shown in Figure 11.

The resonance curves obtained for the large block and the eight small blocks were also the same, as shown in Figure 12. This indicates that both the dynamic stiffness and the internal friction were essentially identical in the two cases.

From this and similar experiments, it became apparent that relative effects caused by changes of size, without change of shape, of rubber mountings

vibrating in compression could be very simply expressed. The same rule of similarity applies for the dynamic stiffness as for the static stiffness.

As regards the internal friction, if α in Equation (2) is multiplied by the factor h/A, where h is the height of the rubber and A the loaded area, a value for the internal friction is obtained which is independent of the size of the rubber test-piece but which depends on the composition and the shape. This value of the internal friction will be designated by η. It corresponds to the coefficient of normal viscosity discussed by Kimball[20]. In the same way, a value for the dynamic modulus can be calculated which is valid for a given shape of test-piece. This is given by:

$$E = sh/A \tag{16}$$

Strictly, this modulus applies only for the same percentage compression, but in many cases the stress-strain curve is sufficiently linear over the limited range of use that any curvature can be ignored.

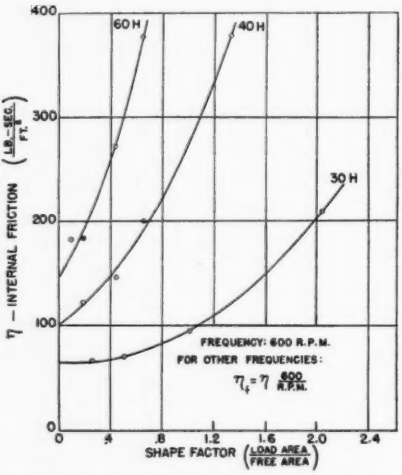

FIG. 13.—Dependence of internal friction on shape.

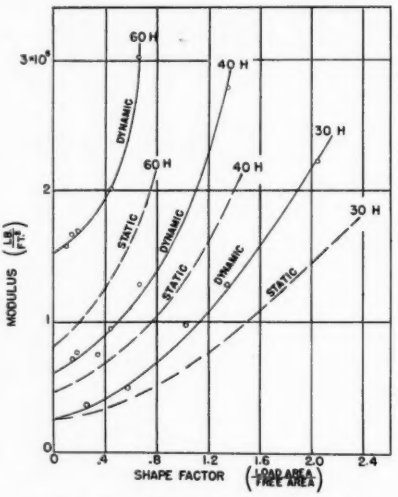

FIG. 14.—Dependence of modulus on shape.

The usefulness of these principles lies in the fact that the determination of E and η for small test-pieces in vibration enables the dynamic properties of full size mountings of similar shape to be calculated. Furthermore, it can safely be assumed that the scale effect for more complicated rubber deformations, such as, for instance, the radial deflections of cylindrical bushings can be handled in the same way.

The effect of shape on the dynamic properties of rubber mountings vibrating in compression is more complicated than the effect of size. Nevertheless, by the use of the shape factor, previously defined and discussed, it is possible to describe the effects in a relatively simple way.

Figure 13 is a plot of η, determined by experiment, against the shape factor for stocks of different durometer hardness. From the curves, the value of η can be read for any desired shape. By use of the relation that the product of η and frequency is constant, which is true at least to a first approximation, the value of η for any frequency can be obtained.

Figure 14 shows curves for E, the dynamic modulus, which is independent of frequency. Curves for the static modulus are also given in Figure 14 for comparison with the dynamic values. The dynamic and static values of the modulus diverge from each other both as the shape factor and durometer hardness increase. Since the design of a mounting usually requires the greatest static stiffness or stability consistent with effective vibration isolation, this deviation of dynamic from static stiffness is in the unfavorable direction and should be taken into account.

Figure 15 is a plot of the internal friction against the dynamic modulus. The relationship between η and E is linear. It should be kept in mind that the variations in η and E are caused by changes in shape of the vibrating piece as shown in the Figures 13 and 14. It thus appears that the increase in modulus with increase in shape factor and the increase in internal friction are both associated with the more complicated stress distribution which occurs at higher shape factors. E and η have also been shown to have a linear interdependence for different pigment loadings[12]. In this case also a complicated stress distribution about the pigment particles may be the controlling factor. Both cases may

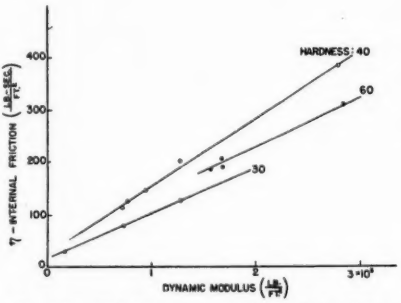

FIG. 15.—Relation between dynamic modulus and internal friction.

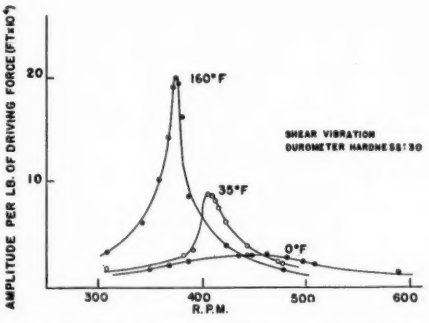

FIG. 16.—Effect of temperature on resonance curves.

be illustrations of the broad general relationship between modulus and viscosity formulated by Gemant[19] on a basis of molecular theory.

From Equation (12) and the linear relationship between η and E, it follows that the dynamic resilience is relatively insensitive to shape factor.

EFFECT OF TEMPERATURE ON RUBBER VIBRATIONS

One of the most important variables affecting the use of rubber mountings is the temperature. Rubber mountings are frequently expected to function over an extended temperature range, so it is important to know the variations of stiffness and resilience which are to be expected.

Rubberlike elasticity for any material is always displayed in a limited temperature range. Vulcanization has the effect of extending this range for raw rubber at both ends; that is, to both lower and higher temperatures. It is thus apparent that a great deal of variation may be expected in the effect of temperature on a rubber composition, depending not only on the added ingredients, such as pigments, softeners, etc., but also on the vulcanization process; that is, the vulcanizing ingredients and the extent of the cure. In spite of this variation, it does seem possible to find some rather general relationships which may be useful.

Figure 16 shows the resonance curves secured for shear vibrations of a commercial mounting stock of 30-durometer hardness, not especially compounded in regard to temperature effects.

Figure 17 shows the temperature dependence of dynamic resilience and dynamic stiffness for this same stock. The values are plotted to show the relative changes from those at 70°F. The data for both dynamic resilience and stiffness are fairly well represented by two straight lines of different slopes, one for the low temperature range and one for the high temperature range. For large shear deformations, where appreciable molecular orientation occurs, an actual

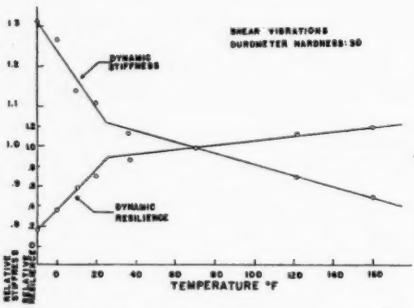

FIG. 17.—Effect of temperature on dynamic properties.

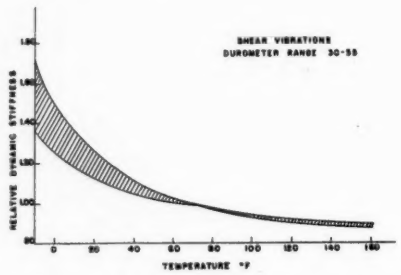

FIG. 18.—Effect of temperature on dynamic stiffness of different rubber compositions.

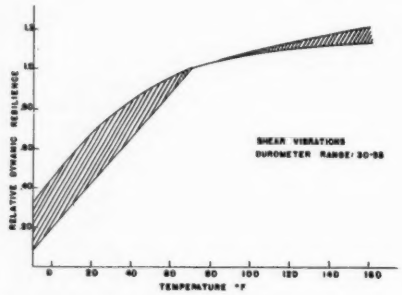

FIG. 19.—Effect of temperature on dynamic resilience of different rubber compositions.

stiffening may be observed as the temperature is raised, analogous to effects with rubber in tension.

Figure 18 is a similar plot of dynamic stiffness, including data secured with commercial mounting stocks with durometer hardnesses in the range 30 to 55. All the values measured fell in the shaded area. The various compositions show a much greater spread in relative temperature effect at low temperatures than at high temperatures. Figure 19 is the same type of plot for dynamic resilience. It is evident that variations in dynamic properties of a mounting caused by low temperatures are likely to be of greater magnitude than those caused by high temperatures. The decrease in resilience and increase in stiffness at low temperature may be even greater than shown here if the rubber is held at the low temperature for a prolonged period of time.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of M. Wendt in the design of the machine and of J. E. Field in the design and construction of the recorder. I also wish to express my thanks to L. B. Sebrell, Manager of the Research Department at Goodyear, for permission to publish this work.

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HEATS OF COMBUSTION AND SPECIFIC HEATS OF BUNA-S TREATED IN VARIOUS WAYS *

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INTRODUCTION

Reliable thermal data on natural rubber[1] have been made available by the work of Jessup and Cummings[2]. These investigators found that the heat of combustion of well purified, natural rubber is 10,767 calories per gram at 30° C in a vacuum, under a constant pressure of 1 atmosphere. On the other hand, there have, to our knowledge, been no investigations of the thermal properties of Buna-S, as manufactured in Germany.

In an effort to make up for this lack of data, the specific heats and heats of combustion of untreated Buna-S, degraded Buna-S, and cyclized Buna-S were measured in collaboration with the I. G. Farbenindustrie-A. G., and Dr. A. Springer, who placed the necessary material at our disposal.

Experimental Procedure

To determine specific heats, strips of Buna were tied together into a bundle by a silver wire, were brought to temperature equilibrium by heating for one-half hour at 50° C in a large test-tube in an aluminum container filled with water, the Buna and test-tube were removed, and were transferred quickly to a heat-insulated silver calorimeter of 350-400 grams capacity. The calibration operation was carried out with cylinders made of pure silver, cadmium or zinc, which were tempered in the same manner, and were transferred to the calorimeter.

In this way, the quantity of heat which is lost in the transfer operation is practically eliminated as a source of error. The average specific heats of the three metals between 20° and 50° C are known reliably. The Beckmann thermometer for the calorimeter and the ordinary thermometer (graduated in tenths of a degree) for the water bath were calibrated accurately. The usual correction was made for the projecting wires, and correction for the heat exchange with the surroundings was made in the ordinary way according to the cooling law of Newton. Stirring was done by hand with a glass stirrer, since no correction was necessary for the heat of stirring. In the calibration with silver, a value of 363.8 calories per degree was obtained with the Beckmann thermometer. The corresponding value with cadmium was 362.7. The uncertainty of the value for water was not, therefore, of any serious concern.

The heats of combustion were determined in an automatically closing Peters bomb made of V_2A steel, and a Peters calorimeter, with side propeller stirrer. The rather large space between the calorimeter and water jacket was divided by a nickel-plated, highly polished, thin-walled sheet-iron cylinder, the object of which was to diminish convection currents. Benzoic acid, succinic acid, and

* Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 17, No. 3, pages 31-33, March 1941.

naphthalene were used for calibration. The operating pressure was 32 atmospheres of oxygen. The value of water was 3575.6 ± 1.65 calories per degree with the Beckmann thermometer. The measurements were carried out at a temperature of almost exactly 20° C. A sample was ignited by a cotton thread, weighing approximately 5 mg., which was tied to a platinum wire. The latter was heated electrically to incandescence. The total correction for the heat of combustion of the cotton thread, the heat of ignition, and the heat of formation of nitric acid[3] amounted to approximately 25 calories, with a total heat exchange of approximately 3500 calories. Any marked differences in the values of the heats of combustion are to be ascribed to lack of uniformity of the material being tested.

With untreated Buna-S and with highly cyclized Buna-S, the uncertainty in the combustion values amounted to only 3 calories in 10,400 calories. The sample with the least degree of uniformity was the highly degraded product designated as sample X.

Sample	Material	Treatment	Hardness (Defo)
I and VIII	Original Buna-S	None. No change in thermal properties in 1.5 months	5000
II	Degraded Buna-S	15 min. in drying oven at 130° C.	3250
III	—	30 min. in drying oven at 130° C.	1650
IV	—	60 min. in drying oven at 130° C.	950
V	—	100 min. in drying oven at 130° C.	700
IX	Technically degraded.	—	2000
X and X′	—	—	400–500
VI	Cyclized Buna-S	120 min. in drying oven at 150° C.	1400
VII	—	350 min. in drying oven at 150° C.	2000
XI	—	450 min. in drying oven at 150° C.	2400

RESULTS

Heats of combustion (calories per gram at 20° C, constant volume).

I	VIII
10,398	10,398
10,391	10,410
10,399	10,384
10,389	10,401
10,391	
$10,394 \pm 2$ average	$10,398 \pm 5$ average

Average $10,396 \pm 3$

If the uncertainty in the value of water is included, the deviation is ± 4 calories, *i.e.*, 0.04 per cent.

II	III	IV	V
10,381	10,309	10,247	10,010
10,390	10,310	10,240	10,033
10,339	10,259	10,260	10,020
10,359	10,262		
$10,367 \pm 12$	10,313	$10,249 \pm 6$	$10,021 \pm 7$
	$10,290 \pm 12$		

After a few weeks the material had become tacky, and gave a still smaller heat of combustion, *viz.*, 9943 calories per gram, as a result of further oxidation by atmospheric oxygen.

VI	10,174	IX	10,329	X′	10,268
	10,172		10,357		10,310
	10,165		10,349		10,085
					10,331
	10,170 ± 3		10,345 ± 8		10,295
					10,258 ± 44
VII	10,231 [4]	X	10,388	XI	10,268
	10,196 [4]		10,388		10,253
	10,192		10,392		
	10,200				10,261 ± 8
			10,389 ± 1		
	10,205 ± 9				

SPECIFIC HEATS

In determining specific heats, the limits of error are considerably greater than in the determination of heats of combustion, because the increases in temperatures are only about 0.2° C. The specific heat of untreated Buna-S hardly changed during storage. On the other hand, cyclized and degraded Buna samples showed notable decreases in specific heat with time.

AVERAGE SPECIFIC HEATS BETWEEN 20° AND 50° C

I and VIII	0.490	VII	0.459	X′	0.451
	0.480				0.439
	0.464	IX	0.468		
	0.473		0.479		0.445 ± 0.006
	0.474		0.452		
	0.462				
	0.464		0.466 ± 0.008		
	0.472 ± 0.004				
VI	0.510	X	0.466	XI	0.471
	0.508		0.463		0.461
	0.509 ± 0.001		0.465 ± 0.002		0.466 ± 0.005

DISCUSSION OF THE RESULTS

In any attempt to calculate the heat of polymerization of Buna-S, it must be borne in mind that this material is not pure simple polymerized butadiene, but that it contains approximately 20 per cent of styrene. Accordingly a mean molecular weight of 64.1 should be used in the calculations. The heat of combustion of liquid styrene is known accurately; it is 10,500 calories per gram at constant volume. The heat of combustion of butadiene vapor has been calculated by the I.G. to be 11,410 calories per gram; that of liquid butadiene is 11,300 calories per gram.

With these values as a basis, calculations show that the heat of polymerization of 64.1 grams of the liquid mixture to crude Buna-S is 41.9 large calories. Jessup[5] made the same calculation for isoprene rubber, and found a considerably lower heat of polymerization, *viz.*, 18 large calories per mol. of isoprene.

In the following work also, the heats of combustion of samples of masticated Buna-S are calculated on a basis of the mean molecular weight of 64.1, although it is fairly certain that some oxygen is taken up and that the molecular weight increases somewhat during the degradation process. In these calculations, the

"molar" heats of combustion are converted in the conventional way to a constant pressure basis.

In the series of samples I to V, the heat of combustion decreased progressively with increase in the extent of degradation, *i.e.*, with increase in absorption of oxygen. Sample X gave an anomalous result.

When a hydrocarbon is transformed into the simplest ketone, *e.g.*, propylene into acetone, the average decrease in the heat of combustion of a noncyclic compound is about 58 large calories; that of a cyclic compound about 52 large calories. In the degradation of crude Buna-S to sample V, one molecule of Buna-S would, if calculated on this basis, consume 0.42 atom of oxygen. In its degradation to sample II, only 0.04 atom of oxygen would be consumed. It would be interesting to determine the heats of combustion of samples of Buna which had taken up accurately known percentages of oxygen. The most highly degraded product (sample X′) appeared to be lacking in uniformity, since in this case the heats of combustion deviated almost 3 per cent. Here then the method of calculation mentioned above is not admissible.

Since the process of cyclization is a reaction which proceeds automatically at moderately high temperatures, heat is evolved in this process, and since there is no change in weight, the heat of combustion must decrease. From the rather scattered data in the literature, it can be calculated that the cyclization of one molecule results in a decrease of approximately 13 large calories in the heat of combustion, but this value is less certain than that for oxygen given above. The difference between the value for untreated Buna-S and that for VI is 14.5 large calories; between untreated Buna-S and that of VII it is 12.2 large calories, and between untreated Buna-S and that of XI it is 8.6 large calories per mol of Buna-S. Here, contrary to expectation, the heat of combustion increases, after an initial decrease, with increase in the degree of cyclization. No explanation can be offered to account for this. It is certain, however, that our results are correct within the limits of error mentioned, so the degree of cyclization would have to be determined to throw further light on the problem.

Hock[6] reports a difference of 116 calories per gram in the heats of combustion of rubber and polycyclorubber; by comparison, the greatest difference in the present work was much larger, *viz.*, 226 calories per gram. The difference between untreated Buna-S and sample XI (135 calories per gram) agrees in an approximate way with the value reported by Hock. This greater difference is to be explained by the absorption of oxygen, either before or during cyclization.

When the heats of combustion were plotted as a function of the deformation, a smooth curve representing the degradation was obtained. To the state of degradation represented by sample IV, the heat of combustion decreased almost linearly as a function of the deformation. Sample X and X′ again showed an anomalous behavior. With the samples of cyclized Buna-S (VI, VII and XI) also, the heats of combustion were an almost straight-line function of the deformation. The heat of combustion as a function of the degradation of Buna-S is shown graphically by Springer[7].

Few reliable values of the specific heat of rubber are available. The most recent value is that reported by Bekkedahl and Matheson[8]. These investigators assign to isoprene rubber a value of 0.4517 calories per degree per gram at 27.5° C. This value is somewhat lower than the value of 0.472 ± 0.004 of untreated Buna-S, found by the present authors. The moderately degraded sample IX showed, within the limits of experimental error, the same specific heat as untreated Buna-S, whereas it would be expected that the introduction of oxygen

into the molecule would lower this value. On the contrary, the specific heats of the highly degraded samples X and X′ are lower than the specific heat of untreated Buna-S, whereas the difference between the specific heats of cyclized sample XI and untreated Buna-S falls within the experimental errors. According to the scanty data in the literature on the influence of cyclization on specific heat, an appreciable decrease was to be expected. The measurements of specific heat should be repeated with larger, strictly fresh samples. A widening of the temperature range would be of no aid since, above 50° C, noticeable changes take place, and these might vitiate the results.

A further discussion from the technical point of view of the results obtained in the present work is to be found in the article by Springer[8].

SUMMARY

Measurements of the heats of combustion and specific heats (between 20° and 50° C) of crude untreated Buna-S, highly degraded Buna-S, and cyclized Buna-S are reported. The heats of combustion are then discussed. A well defined relation exists between thermal data and changes which take place in Buna-S. In the case of specific heats, the values of which are less precise, the relation is not so clearly defined.

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[2] Jessup and Cummings, *J. Research Natl. Bur. Standards* **13**, 357 (1934).
[3] In the combustion, aqueous nitric acid is formed by the reaction of nitrogen, oxygen and water at local points where the temperature reaches as high as 1800° C, according to the scheme: $0.5\ N_2 + 2.5\ O_2 + 0.5\ H_2O$ + water → aqueous HNO_3. This reaction has a heat tone of +14 large calories per mol. The nitric acid which is formed is determined by titration with sodium hydroxide.
[4] These determinations were made in a microbomb.
[5] Jessup, *J. Research Natl. Bur. Standards* **20**, 596 (1938).
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DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF THE SYSTEM RUBBER-CALCIUM CARBONATE *

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INTRODUCTION

A study of the electrical properties of rubber-filler systems has been undertaken by the National Bureau of Standards for the purpose of arriving at general relations for the effect of typical fillers on the dielectric constant, power factor, and conductivity of rubber compounds containing the fillers. It is intended that the investigation be comparable in scope to the previous study of the system rubber-sulfur[1]. A portion of the work dealing with calcium carbonate as a filler has been completed, and is presented here.

The term "rubber" has been rather broadly construed in connection with these studies to include not only conventional vulcanized natural rubber, but also synthetic rubberlike materials. Thus, specimens made from Vistanex, a high molecular-weight polymer of isobutylene, have been included in the present work. The experimental compounds which were prepared are simpler than any which would be employed in practice, the aim being to look for general relations rather than to develop practical insulating compounds.

PREPARATION OF THE SPECIMENS

The specimens were made by adding calcium carbonate to the base compounds in a series up to about 50 per cent by volume. The composition was closely controlled, and special attention was paid to the moulding of the specimens so as to obtain the high degree of uniformity in thickness requisite for the accurate determination of the electrical properties.

COMPOSITION AND MIXING OF THE EXPERIMENTAL COMPOUNDS

One base compound was made from natural rubber according to the following formula:

Ingredients:	Parts by weight
Blended smoked sheet rubber	100
Zinc oxide (Kadox)	1
Stearic acid	2
Tetramethylthiuram disulfide	3
	106

The natural rubber had been blended before purchase so as to give a uniform grade of rubber for test purposes. This base compound and the calcium carbonate compounds prepared from it were vulcanized for 30 minutes at 126° C.

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The other base compound consisted of high molecular-weight Vistanex. Vistanex is a polymer of isobutylene, produced in the United States by the Advance Solvents and Chemical Corporation. The Vistanex compounds, of course, required no vulcanization. They were of such consistency that specimens could be moulded to precise dimensions. They had the advantage over rubber specimens that they could be remoulded repeatedly if they were imperfect or not of the desired shape.

The calcium carbonate used in the investigation was of the reagent grade, and of the type low in alkalies.

The maximum limit of impurities was 0.5 per cent for magnesium and 0.08 per cent for all other impurities. It was assumed that the magnesium carbonate was similar to calcium carbonate in its effect on the electrical properties, and that the other impurities were present in too small amounts to be of significance.

The compounds were usually mixed in a laboratory internal mixer. The mixer was not perfectly tight, so that some of the calcium carbonate was lost by dusting; batches were weighed before and after the addition of this material and the loss was made up. The vulcanizing agent, tetramethylthiuram disulfide, was added on a roll mill, as is the usual practice.

The accuracy of the compounding was checked by determining the specific gravity of the finished specimens, and, in the case of the Vistanex compounds, the residue on ignition was determined as a further check. Vistanex, unlike natural rubber, can be driven off at a temperature below red heat, and hence well below the temperature at which calcium carbonate undergoes significant decomposition.

Moulding and Vulcanizing of the Specimens

Special care was necessary to mould the specimens so that they would be free from entrapped air and would be sufficiently uniform in thickness to permit the determination of dielectric constant to be made to the desired accuracy. Two forms of specimens were used. Some of the specimens were prepared in the form of discs having embedded aluminum electrodes, whereas the rest were prepared in the form of rectangular slabs, to which foil electrodes were subsequently applied.

The disc-shaped specimens were similar to those employed in a previous investigation[1], where one embedded electrode was smaller than the other. The present specimens were made considerably thicker in an effort to improve the precision with which the effective thickness could be measured. The method of measuring thickness is described in a subsequent section of this paper. The electrodes were 15 cm. and 20 cm. in diameter, respectively, and the thickness of the rubber was about 0.6 cm. When these specimens were moulded and vulcanized in a single operation, they were somewhat thicker at the center than at the edges, or slightly lens-shaped. To obviate this difficulty, the stock was first moulded in the form of a blank at about 100° C. After the electrodes had been applied, it was again moulded at 100° C. The temperature was then raised to 126° C, and the specimen vulcanized. By thus separating the moulding and vulcanizing operations, it was possible to obtain specimens highly uniform in thickness.

When specimens having embedded electrodes were being prepared, blanks of the stock were usually made and allowed to stand for several days before they were moulded to the final shape. This was done to get rid of air, which is often entrapped in compounds containing large proportions of filler. In form-

ing the blanks, any air pockets are collapsed by the high pressure, and the air is forced into solution. When the pressure is released the air remains in the form of a supersaturated solution which diffuses slowly to the surface and escapes if no electrodes are present. If electrodes have been applied before the air has had time to escape, it accumulates in pockets underneath them.

The rectangular specimens were about 16 cm. long, 15 cm. wide, and 0.6 cm. thick. Tinfoil electrodes were made to adhere to the specimens, using a thin film of vaseline as an adhesive, by rolling the tinfoil down with a narrow roller. This gave tightly adhering electrodes, since the small amount of vaseline left was absorbed by the rubber. One electrode was made to cover an entire face, the opposite one was cut to a rectangle 11 by 12 cm. The vaseline used in applying the tinfoil electrodes probably did not affect the electrical properties of the specimens, since comparative measurements made with embedded aluminum electrodes and tinfoil electrodes agreed within experimental error.

Examination of Specimens for Porosity

The specimens were carefully examined for porosity, since the presence of voids, or air pockets, would decrease the accuracy of the electrical determinations. Large defects in the specimens having embedded electrodes were usually evident by a variation in thickness. Typical specimens were cut up after the electrical measurements had been made, and the cut edges of the compound were examined for pores. When defects were found in any specimen, the measurements on that specimen were discarded.

To investigate the possibility that the specimens might be more porous than visual inspection would indicate, compressibility measurements were made on strips cut from representative specimens. Volume compressions at 1,500 and 3,000 lbs. per sq. cm. pressure were determined. If no air pockets were present, the volume compression at 3,000 lbs. per sq. cm. should be approximately twice that at 1,500 lbs. per sq. cm. Large deviations from this can be attributed to air pockets which are collapsed at the lower pressure.

To make the volume compression measurements, the specimen strips were placed in a Pyrex-glass piezometer having the form shown diagrammatically in Figure 1. When this was placed under pressure in a pressure bomb, mercury was forced through the fine capillary in the bottom and dropped off the tip inside, thus being trapped. After the pressure was released, this mercury was weighed. From a knowledge of the weight of the mercury, the volume of the capillary, the compressibility of the glass, the volume of the piezometer, and the volume of the specimen, the volume compression ($K=\Delta V/V_0$) of the specimen could be determined.

After the volume compressions for 1,500 and 3,000 lbs. per sq. in. pressure had been determined, the fraction of the volume (U) of the specimen occupied by air pockets was computed from:

$$U=K'-\left(\frac{K''-K'}{P''-P'}\right)P', \tag{1}$$

where K' is the volume compression for pressure P' (1,500 lbs. per sq. in.) and K'' is the volume compression for pressure P'' (3,000 lbs. per sq. in.). This assumes that the compressibility of the specimen does not vary with the pressure. Since the compressibility decreases somewhat with pressure, the values thus obtained are higher than the actual values. However, the error is not large, and

if the computed value is below the allowable limit, the actual value certainly is. All the specimens in this work which were not discarded as a result of visual inspection contained less than 0.4 per cent by volume of air. Since the thickness cannot be measured more closely than 1 per cent, it was assumed that air volumes of 1 per cent could be tolerated. The specimens were well within this limit.

MEASUREMENT OF DIMENSIONS OF THE SPECIMENS

The thickness of each of the circular specimens having aluminum electrodes was measured by means of the tilting-bar gauge described in a previous publication[1]. The overall thickness was measured at a number of points according to a fixed pattern, and from this the combined thickness of the two electrodes was subtracted. The area of the specimen was taken as the area of the smaller electrode. The diameter of the smaller electrode was measured by means of a steel rule.

The thickness of each of the rectanguglar specimens was determined from the volume obtained by means of hydrostatic weighings. The edges were cut straight by means of a knife working in a guide, a strip about 0.6 cm. wide being cut from each edge. The length and breadth were then measured by means of a steel rule, and the area was computed. From the area thus obtained and the volume found by hydrostatic weighing, the average thickness was computed. A few of the specimens were measured for uniformity of thickness, using a gauge designed by Holt[2], which applied very light pressures to the specimen. The area used in computing the dielectric constant was that of the smaller electrode, and this was computed from measurements of the length and breadth made with a steel rule.

ELECTRICAL MEASUREMENTS

Dielectric Constant and Loss Tangent of the Rubber Compounds

The capacitance and loss tangent (tangent of the phase difference angle, *i.e.*, tan δ)[3] of the specimens were measured on a conjugate Schering bridge similar to the one described in the American Society for Testing Materials standard method for measuring capacitance and power factor[4]. A diagram of the bridge is shown in Figure 2. The entire bridge, with the exception of the transformer supplying the power, was enclosed in a grounded metallic cage which was large enough to accommodate the operator. The four arms of the bridge are indicated by the subscripts 1, 2, 3, 4, and the Wagner round is indicated by the subscripts 5 and 6. The variable resistor, R_g, when properly adjusted, aided in the balance of the bridge[5]. The function of this resistance in the bridge balance has been discussed by Astin in his detailed analysis of the bridge[6].

In making a measurement of capacitance and loss tangent, several cycles of adjustment were necessary in which the detector was connected first to the bridge and then to ground. The specimen (C_x) was connected into the bridge by closing switch S_a to 1. A cycle of adjustments consisted of closing switch S_b to 1 and balancing the bridge by adjusting C_2 and C_3, then throwing switch S_b from 1 to 2 and balancing the bridge by adjusting C_5 and R_5. This cycle was repeated until throwing switch S_b from 1 to 2 did not affect the balance.

Convergence to balance was made more rapid by the proper adjustment of R_g. This adjustment was made after one or two cycles of adjustment, as described above, and needed to be made only once, as long as specimens of about the same capacitance were measured. The adjustment of R_g was made as follows. With the balance obtained when the switch S_b was thrown to 1, as described

above, R_5 was set sufficiently off balance to give a good indication in the detector. R_g was then adjusted for a minimum detector indication. The regular cycles of adjustment for balance were then continued.

When the bridge had been properly balanced, readings of C_2 and C_3 were taken. Call them C_2' and C_3', respectively. The specimen was then disconnected

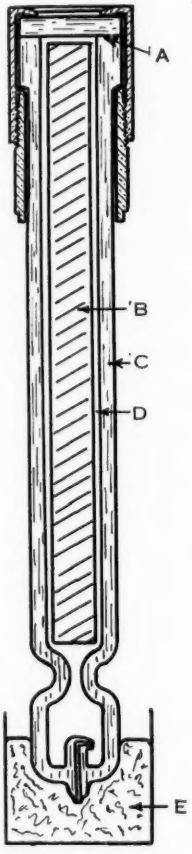

FIG. 1.—Piezometer for measuring volume compressions of rubber specimens.

A, lapped surface; *B*, specimen; *C*, Pyrex glass; *D*, confining liquid; *E*, mercury.

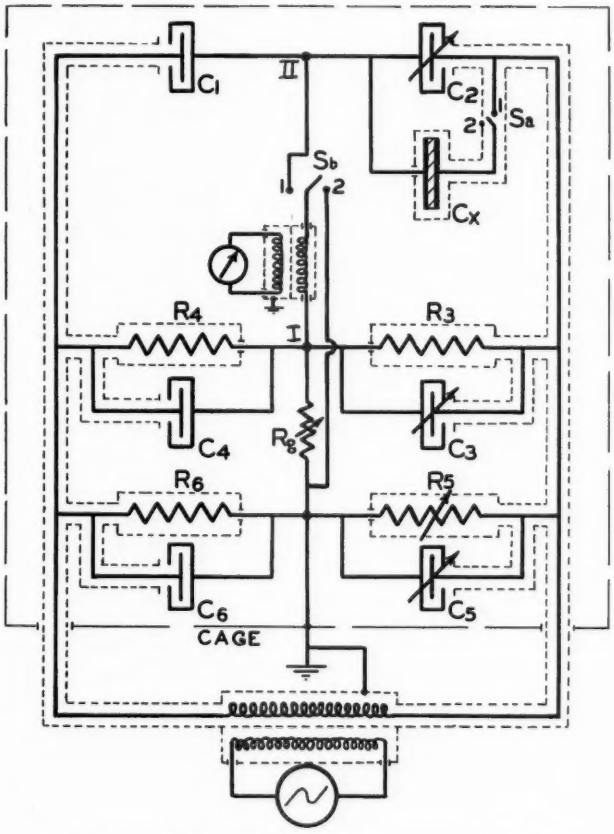

FIG. 2.—Conjugate Schering bridge for measurements of capacitance and loss tangent.

by throwing switch S_a to 2. The bridge was adjusted as before without disturbing R_g, and the readings of C_2 and C_3 were again taken. Call them C_2'' and C_3'', respectively. The capacitance, C, was then computed by means of the equation:

$$C = C_2'' - C_2'. \tag{2}$$

The edge capacitances were determined by the method described in a previous paper[7] for computing the edge capacitance from the perimeter of the smaller

electrode and the thickness of the specimen. Thus the dielectric constant, K, of the material is given by:

$$K=\frac{C-C_i}{C_n+C_m}, \tag{3}$$

where

C = the measured capacitance of the specimen in micromicrofarads

$$C_i=\frac{P}{30}\ln\frac{3.8}{b}$$

$$C_n=\frac{1.113A}{4\pi b}$$

$$C_m=.0405P$$

P = perimeter of the small electrode in centimeters

b = thickness in centimeters, and

A = the area of the small electrode in square centimeters.

It was shown in the previous paper[7] that C_i was independent of the dielectric constant of the material and was, therefore, presumably the capacitance in air at the edge of the electrodes, so the loss tangent of the material, tan δ_x, is given by:

$$\tan\delta_x=\frac{\omega R_3 C_2'(C_3''-C_3')}{C-C_i}, \tag{4}$$

where ω is 2π times the frequency, and R_3 is the resistance in parallel with C_3.

Equations 2 and 4 are not exact, but give the values with sufficient approximation if the loss tangent of the specimen is less than 0.1, and if the loss tangent of the standard capacitor, C_2, can be considered to be zero. The specimens were measured at two frequencies, namely, 1 kilocycle per second and 100 kilocycles per second.

Dielectric Constant of Calcium Carbonate

The dielectric constant of the calcium carbonate was found by two different methods. One method, which is described in another paper[8], consisted in making direct measurements on specimens of white marble in the form of flat discs. In the other method, various mixtures of two liquids, one of which had a higher dielectric constant and the other a lower dielectric constant than the powder to be measured, were prepared. The powder was added to these liquid mixtures, and the effect of the powder on the dielectric constant of the mixtures determined. The dielectric constant of the powder is the same as that of the liquid when the dielectric constant of the mixture of powder and liquids is the same as that of the liquid mixture alone. Some of the more recent descriptions of this method are given by Luca, Campbell, and Maass[9], Whitehead and Hackett[10], Cheng[11], and Wachholtz and Franceson[12]. Actually, the liquid mixture having a dielectric constant exactly that of the calcium carbonate was not prepared, as this would have been too tedious. The value of the dielectric constant of the calcium carbonate was obtained by interpolation.

A number of liquid mixtures were prepared, each having a different proportion of the two liquids, benzene, and nitrobenzene. The dielectric constants of these liquid mixtures were determined by means of a cylindrical cell, which is shown in cross-section in Figure 3. This cell was calibrated by means of benzene, the dielectric constant of which is known. The level of the liquid in the cell was

kept to a mark on the inside of the cell. After the dielectric constant of the liquid mixture had been determined, 20 grams of calcium carbonate powder was added to the liquid mixture in the cell. The excess liquid was removed from the cell to bring its level again to the mark, and the change in capacitance of the cell was determined. The percentage changes in capacitance were then plotted against the dielectric constants of the liquid mixtures, and a curve was

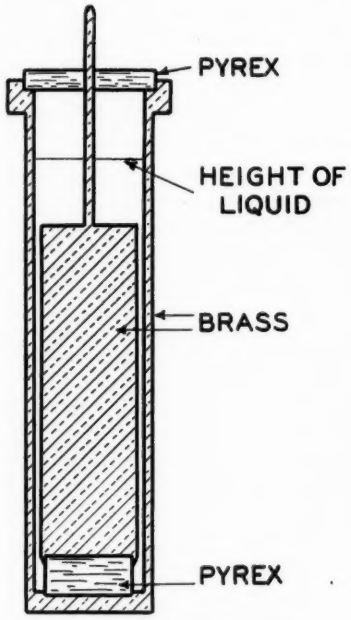

FIG. 3.—Cylindrical cell for measuring the dielectric constants of powders.

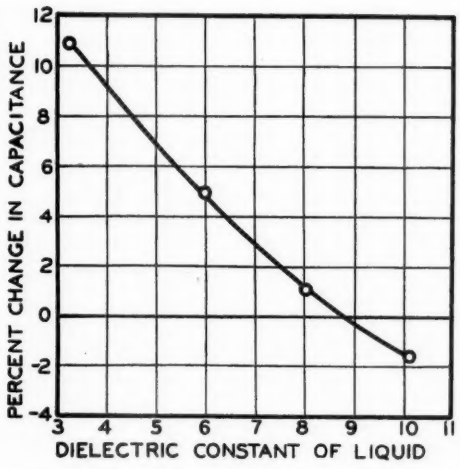

FIG. 4.—Curve for determining the dielectric constant of calcium carbonate powder.

The points are values of the percentage change in the capacitance of the cell when the powder was added to the liquid. The dielectric constant of the powder was taken as that of the liquid where the curve crossed the zero line.

drawn through the points, as shown in Figure 4. The point where the curve crosses the zero ordinate line gives the dielectric constant of the calcium carbonate.

CONDUCTANCE

The conductance of the specimens was determined from measurements made either with a highly sensitive galvanometer used as an ammeter, as described in a previous paper[1], or by means of an electrometer tube circuit similar to the one described by Penick[13]. In the latter case, a Western Electric electrometer tube was used.

A diagram of the electrometer tube circuit is shown in Figure 5. The circuit is so arranged that effects of fluctuations in the filament current are minimized. The circuit was balanced to give zero deflection of the galvanometer, G, in the following way. The current through the filament was adjusted to the rated

value (0.27 ampere) by adjusting R_4. Resistor R_5 had been so chosen that this current flowing through it gave the proper negative bias (3 volts) to the grid. The resistance of R_3 was so chosen that a potential difference of about 8.5 volts existed between A and B. With the grid at -3 volts and the galvanometer, G, disconnected, the slider on R_3 was adjusted until the potential between A and C was about 5.3 volts. R_1 was then adjusted until the potential between A and D was about 4 volts. Next, the galvanometer was connected, and R_2 was adjusted until the galvanometer deflection was zero. R_4 was then changed so that the filament current was slightly altered. If this deflected the galvanometer, the slider on R_3 was not in the correct position, and it therefore was moved

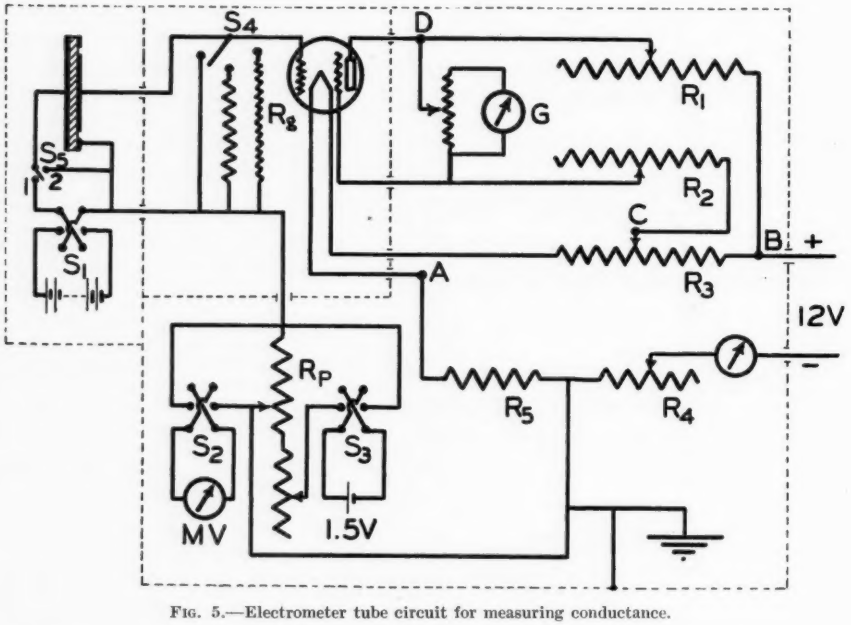

FIG. 5.—Electrometer tube circuit for measuring conductance.

slightly in one direction. The galvanometer deflection was again brought to zero by adjusting R_2. If this decreased the effect of a slight change of R_4 on the galvanometer deflection, the slider on R_3 was moved still farther in the same direction. If it increased the effect, then the slider was moved in the opposite direction. This adjustment was continued until a slight change in the filament current did not affect the galvanometer deflection.

To make a determination of conductance, switch S_5 was thrown to 1, thus connecting the specimen into the circuit, S_4 was connected to the proper grid resistor, and S_1 was closed in one direction. The current which flowed through the specimen also flowed through the grid resistor, R_g, and thus caused a potential difference between the ends of the resistor. Since the grid of the electrometer tube was connected to one end of the grid resistor, a potential was applied to the grid, which caused a deflection of the galvanometer, G. The deflection of the galvanometer was noted at the end of 1 minute. The potential due to the specimen current flowing through the resistor, R_g, was then removed from the grid and an equal potential applied which could be measured. To do

this, switch S_1 was opened and S_4 was turned to the contact which had no resistance connected to it. Switch S_5 was thrown to 2 to short the specimen and guard to the opposite electrode. A potential was applied to the grid of the tube by closing switch S_3 in such a direction that the deflection of the galvanometer was the same as before. The potentiometer, R_p, was then adjusted until the magnitude of the deflection was the same as before, which indicated that the potential applied to the grid of the tube was the same as before. This potential was measured by means of a millivoltmeter connected to switch S_2. After the specimen had been shorted at least 2 minutes, a second measurement was made with switch S_1 closed in the opposite direction. An average of the two readings of the millivoltmeter was taken for computing the conductance. The conductance, G_x, of the specimen is given by:

$$G_x = \frac{GE_g}{E_x}, \tag{5}$$

where G is the conductance of the grid resistor, R_g, E_g is the average reading of the millivoltmeter, and E_x is the potential applied to the specimen.

RESULTS

The values of dielectric constant, loss tangent, and conductivity (at end of 1 minute of electrification) for mixtures containing calcium carbonate are given in Tables I, III, and IV. The first column of each table gives the base materials with which the calcium carbonate was mixed. The second column gives the percentages of calcium carbonate by volume in the mixture. The maximum, minimum, and mean values of each property are given, as are the number of determinations made. The values of dielectric constant and loss tangent are given for two frequencies.

Dielectric Constant

The dielectric constant values in Table I were plotted against the percentages of calcium carbonate by volume, as shown in Figure 6, where the measured values are represented by circles. Only the values at 1 kilocycle per second are shown in the figure, since there is only a small difference between the values at the two frequencies.

The value 8.75 used for the dielectric constant of calcium carbonate is the one obtained for the powder by the method of liquid mixtures. This value is about 2 per cent higher than the value (8.57) obtained for the dielectric constant of the white marble[8]. The value 8.75 was used in spite of the fact that it was determined by a less precise method, because it was obtained on a sample of the powder that was used in preparing the specimens.

Many formulas have been proposed for representing the dielectric constants of mixtures. Lichtenecker[14] and also Wachholtz and Franceson[12] have considered most of them and have given comprehensive discussions of their limitations. A few of the most promising of these were tested to see if they would fit the present data. Two formulas agreed with the data sufficiently well to warrant consideration.

One of these formulas was developed by Wiener[15] for the conductivity of mixtures. Since the formula for conductivity involves the dimensions of the specimens in the same way as the formula for dielectric constant, either may

TABLE I

DIELECTRIC CONSTANT OF MIXTURES CONTAINING CALCIUM CARBONATE AS A FILLER

Base material	Volume of calcium carbonate	Number of determinations	Dielectric constant at 1,000 c/s			Dielectric constant at 100,000 c/s		
			Maximum	Minimum	Mean	Maximum	Minimum	Mean
	%							
Natural rubber	0	8	2.54	2.49	2.52	2.54	2.48	2.51
Natural rubber	10.2	2	2.91	2.90	2.91	2.89	2.88	2.89
Natural rubber	23.3	6	3.47	3.44	3.46	3.44	3.42	3.43
Natural rubber	32.1	3	3.92	3.90	3.91	3.88	3.86	3.87
Natural rubber	49.6	3	4.84	4.83	4.83	4.80	4.78	4.79
Vistanex	0	4	2.29	2.29	2.29	2.29	2.29	2.29
Vistanex	10.0	3	2.63	2.62	2.63	2.63	2.61	2.62
Vistanex	24.6	3	3.26	3.24	3.25	3.25	3.22	3.23
Vistanex	35.7	4	3.85	3.84	3.85	3.84	3.83	3.84
Vistanex	47.7	2	4.58	4.56	4.57	4.55	4.53	4.54
Marble *	—	8	8.64	8.55	8.57	—	—	—
Calcium carbonate powder	—	—	—	—	8.75	—	—	—

* Values taken from a former paper[8].

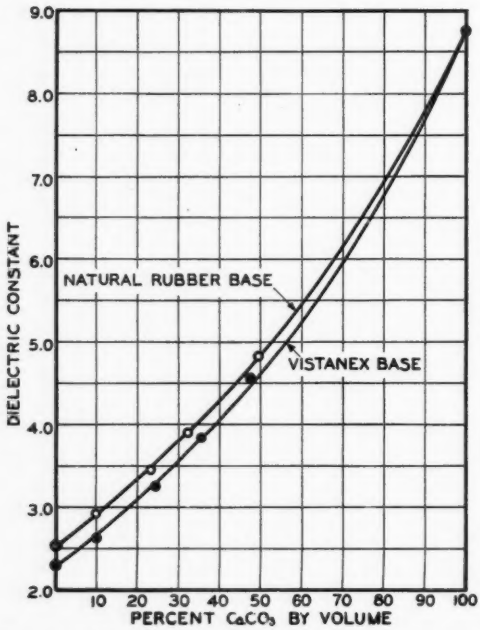

FIG. 6.—Dielectric constant of rubber containing calcium carbonate at 1 kilocycle per second.

The points represent experimental values and the curves are given by Equation 7.

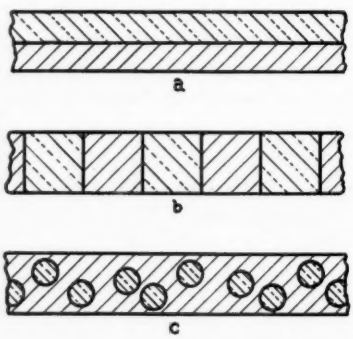

FIG. 7.—Distribution of components for Formula (7).

(a) Series distribution, $F = 0$.
(b) Parallel distribution, $F = \infty$.
(c) Spheres embedded in continuous phase, $F = 2$.

The two components are distinguished in each case by the different slopes of the cross-hatching.

be used in the Wiener formula. Using the dielectric constant, the formula becomes:

$$\frac{K-K_1}{K+FK_1}=V_2\frac{K_2-K_1}{K_2+FK_1} \tag{6}$$

or

$$K=\frac{K_1[K_2+FK_1+V_2F(K_2-K_1)]}{K_2+FK_1-V_2(K_2-K_1)}, \tag{7}$$

where K, K_1, and K_2 are the dielectric constants of the mixture, continuous phase (rubber), and the dispersed phase (calcium carbonate), respectively, V_2 is the volume fraction of the dispersed phase, and F is a characteristic constant. If $F=0$, we have the series distribution of the components, as shown diagrammatically in Figure 7(a). If $F=\infty$, we have the parallel distribution of the components, as shown diagrammatically in Figure 7(b). If $F=2$, we have the formula developed by Maxwell for spheres embedded in a continuous medium, as illustrated in Figure 7(c).

Formula 6 was developed independently by Fricke[16], who computed the values that F should have for certain ellipsoidal shapes of the embedded particles. If the particles are flattened and their short axes are parallel to the field, F has a value less than 2 but greater than 0, whereas if the short axes are perpendicular to the field, F has a value greater than 2.

Wachholtz and Franceson[12] investigated the dielectric constants of mixtures of paint pigments in linseed oil. They found that the shape of the particles had a decided effect on the dielectric constant of the mixture. They found also that F was essentially constant with variations in the powder content for those powders whose particle shapes did not differ too radically from the symmetrical shape. Since the particles had random orientation, they found that F was always larger than 2 if the particle deviated from the symmetrical shape. Thus for barite, which had cubical particles (the space arrangement is not very different for spheres and cubes), the value of F was 2, but for zinc sulfide, which had elongated particles, the value of F was 3.8.

Applying Equation 6 to our present data, we can solve for F and get values of F for the various percentages of the calcium carbonate in the rubber. Thus we have:

$$F=\frac{V_2K(K_2-K_1)-K_2(K-K_1)}{K_1(K-K_1)-V_2(K_2-K_1)}. \tag{8}$$

The values of F computed by means of Formula 8, using the data in Table I, are given in Table II. The values of F for the rubber base are probably constant within experimental error, but there is a definite increase with filler content for the Vistanex base. By giving more weight to the values obtained with higher filler contents, it seems that 2.7 is the most probable value of F. Using this value of F, the dielectric constant values were computed for varying percentages of calcium carbonate for both Vistanex and natural-rubber bases. The curves shown in Figure 6 represent the computed values. The points represent the measured values. The values of dielectric constant for the percentages of fillers used in the specimens are given in the fifth column of Table II. The agreement between the measured and computed values for the specimens having the natural-rubber base is very good, *i.e.*, the difference is less than 1 per cent. The agreement is not quite so good for the specimens having the Vistanex base, but

the differences between the measured and computed dielectric constants are less than 2 per cent.

According to the work of Wachholtz and Franceson[12], the amount by which the value of F exceeds 2 is a measure of the elongation of the particles. Since this difference for calcium carbonate is 0.7, the indication is that the particles of calcium carbonate are elongated somewhat.

TABLE II

COMPUTED VALUES OF F AND K FOR 1,000 CYCLES PER SECOND

Base material	Volume of calcium carbonate	K (measured)	F (computed by Equation 8)	K (computed by Equation 7, using $F = 2.7$)	K (computed by Equation 9, using $x = 0.2$)
Natural rubber	0	2.52	—	2.52	2.52
Natural rubber	10.2	2.91	2.5	2.92	2.90
Natural rubber	23.3	3.46	2.5	3.48	3.47
Natural rubber	32.1	3.91	2.8	3.90	3.89
Natural rubber	49.6	4.83	2.7	4.83	4.85
Vistanex	0	2.29	—	2.29	2.29
Vistanex	10.0	2.63	1.7	2.67	2.66
Vistanex	24.6	3.25	1.9	3.30	3.30
Vistanex	35.7	3.85	2.8	3.84	3.85
Vistanex	47.7	4.57	3.2	4.49	4.54
Calcium carbonate powder	—	8.75	—	8.75	8.75

TABLE III

LOSS TANGENT OF MIXTURES CONTAINING CALCIUM CARBONATE AS A FILLER

Base material	Volume of calcium carbonate (percentage)	Number of determinations	Loss tangent: At 1,000 c/s — Maximum	At 1,000 c/s — Minimum	At 1,000 c/s — Mean	At 100,000 c/s — Maximum	At 100,000 c/s — Minimum	At 100,000 c/s — Mean
Rubber	0	8	26×10^{-4}	19×10^{-4}	22×10^{-4}	34×10^{-4}	30×10^{-4}	32×10^{-4}
Rubber	10.2	2	27	27	27	24	23	24
Rubber	23.3	6	32	26	28	33	27	30
Rubber	32.1	3	36	35	36	37	36	36
Rubber	49.6	3	34	33	34	30	29	30
Vistanex	0	4	2	1	2	4	3	3
Vistanex	10.0	3	4	3	3	4	4	4
Vistanex	24.6	4	20	11	13	7	6	6
Vistanex	35.7	4	16	11	14	9	8	9
Vistanex	47.7	2	19	14	17	11	11	11
Marble *	—	8	56	10	22	—	—	—

* Values taken from a former paper[8].

The other formula which gave values agreeing well with the measured values of dielectric constant was:

$$K^x = V_1 K_1^x + V_2 K_2^x, \tag{9}$$

where K, K_1, and K_2 are the dielectric constants of the mixture, the continuous phase, and the dispersed phase, respectively, V_1 and V_2 are the volume fractions of the continuous phase and the dispersed phase, respectively, and x is a constant.

The value of x that fitted the data most closely was found by the method of trial and error to be 0.2. Using this value of x, the values of the dielectric constant were computed by means of Formula 9 for the percentages of calcium

carbonate used in the specimens. These values, which are given in the sixth column of Table II, agree with the measured values as well as did the values computed by means of Formula 7. Although Formulas 7 and 9 give values which agree about equally well with the measured values, Formula 7 may be preferred, since it gives some indication of the shape of the particles and state of dispersion of the powder.

Loss Tangent

The values of loss tangent at 1,000 cycles per second given in Table III are plotted in Figure 8 against the percentages of calcium carbonate by volume. The vertical lines through the points indicate the spread in values. Since the data in Table II indicate practically no change with frequency for the speci-

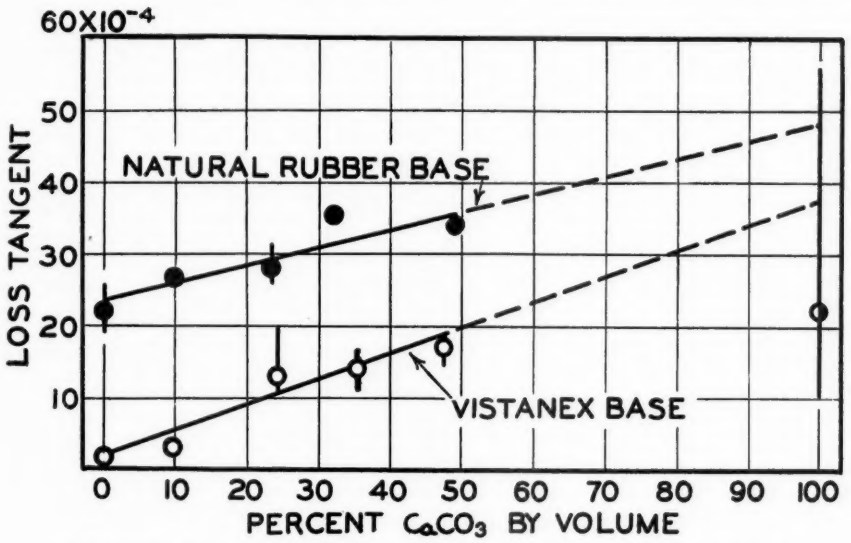

Fig. 8.—Loss tangents of rubber containing calcium carbonate at 1 kilocycle per second. The vertical lines through the points show the spread of values.

mens containing a natural rubber and a small decrease with frequency for the specimens containing Vistanex, values for only the one frequency have been plotted. The loss tangent appears to increase directly with the percentage of calcium carbonate by volume. The straight lines drawn through these points and extended to 100-per cent calcium carbonate would indicate a value for the loss tangent of calcium carbonate higher than the average value obtained for the marble. However, the extrapolated values lie within the range of values obtained, so it can be assumed that the loss tangent is directly proportional to the calcium carbonate content.

Conductivity

The conductivity was determined at the end of 1 minute of electrification, and is called the "1-minute" conductivity. The logarithms of the values of the 1-minute conductivity given in Table IV are plotted in Figure 9 against the calcium carbonate content. The vertical lines through the points indicate the

spread of the values. The conductivities of the two base compounds are quite different, that of the natural rubber compound being about 50 times that of Vistanex. The curves of the two (solid lines) are also quite different. The conductivity of the specimens containing natural rubber passes through a minimum, whereas that for Vistanex increases continuously with increasing calcium carbonate content.

Since Equation 7, which fitted the dielectric constant data so well, was originally developed for conductivity, it is of interest to see how it fits the measured values of conductivity. Substituting conductivities for dielectric constants:

$$\frac{\gamma-\gamma_1}{\gamma+F\gamma_1}=V\frac{\gamma_2-\gamma_1}{\gamma_2+F\gamma_1}, \tag{10}$$

where γ is the conductivity of the mixture, γ_1 the conductivity of the rubber, γ_2 the conductivity of the calcium carbonate, V the volume fraction of the calcium carbonate, and F a characteristic constant. The dashed curves of

TABLE IV

CONDUCTIVITY OF MIXTURES CONTAINING CALCIUM CARBONATE AS A FILLER

Base material	Volume of calcium carbonate	Number of determinations	"One-minute" conductivity, in mho-cm^{-1}		
			Maximum	Minimum	Mean
Natural rubber	0	8	160×10^{-17}	39×10^{-17}	88×10^{-17}
Natural rubber	23.3	6	37	23	28
Natural rubber	32.1	3	22	22	22
Natural rubber	49.6	3	28	23	26
Vistanex	0	2	2.0	2.0	2.0
Vistanex	10.0	7	7.2	3.5	4.9
Vistanex	24.6	2	170	48	92
Vistanex	35.7	2	320	190	260
Marble *	—	8	4,800	290	990

* Values taken from former paper[8].

Figure 9 represent the values computed by means of Equation 10, using the value of 2.7 for F. These values do not agree with the data for 1-minute conductivity. The conductivities for specimens containing Vistanex were much higher than the computed values, while for those containing natural rubber they were much lower. Apparent that the 1-minute conductivity is not a direct result of structure but is caused by secondary effects.

In considering the conductivity of a dielectric, it must be kept in mind that the conductivity at the end of 1 minute is a purely arbitrary determination. Rubber compounds usually have considerable electrical absorption, which means that the current flowing through the specimen under constant potential decreases with time, rapidly at first, then more slowly. Thus the conductance which is determined will depend on the time at which the current was measured. Since different specimens may exhibit different electric absorption curves, the conductances determined for a fixed time of electrification may not be comparable. This may explain why the measured values do not agree with the computed values.

SUMMARY

The results obtained in this investigation indicate that either the formula developed by Wiener (Formula 7) or the exponent formula (Formula 9) may

be used for the computation of the dielectric constants of mixtures of calcium carbonate and rubber. Formula 7 may be preferred, since it gives some indication of the shape of the particles and state of dispersion of the powder.

There was little difference between values of the dielectric constant and loss tangent at 1 kilocycle per second and at 100 kilocycles per second.

The change of the loss tangent with the content of calcium carbonate was

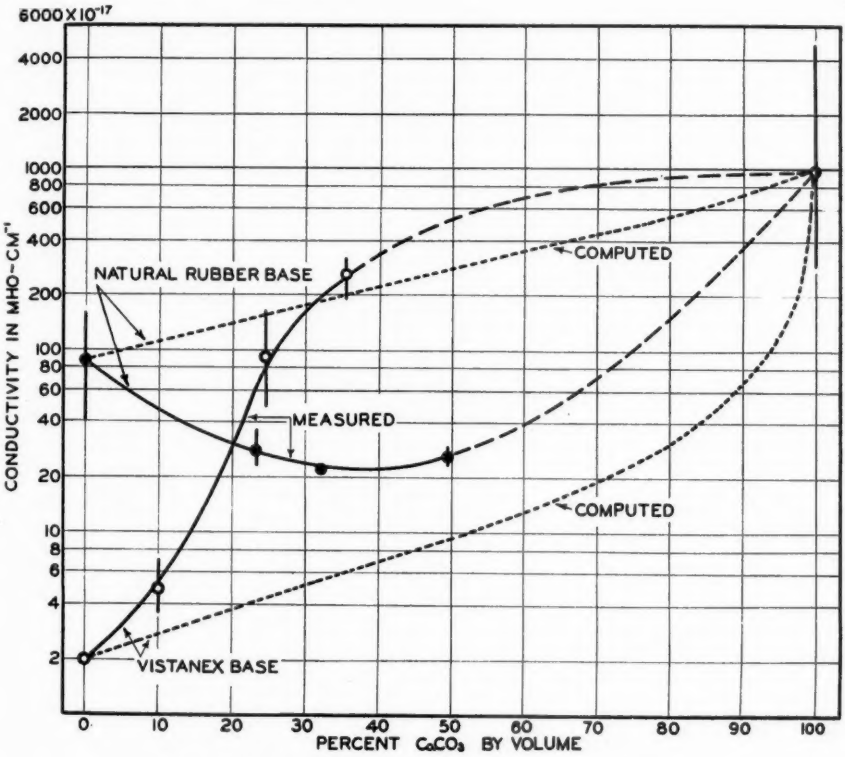

FIG. 9.—Conductivity of rubber containing calcium carbonate.

The vertical lines through the points show the spread of values. The solid line curves were obtained from Equation 10.

not large, but a direct relationship between loss tangent and percentage of calcium carbonate was indicated.

The 1-minute-conductivity values increased continuously with increasing content of calcium carbonate when Vistanex was used as the base, but passed through a minimum when natural rubber was used.

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[2] Holt, *Bur. Standards J. Res.* **10**, 575 (1932).
[3] The term loss tangent is used throughout this paper rather than power factor because the loss tangent comes directly from the bridge equations. For values less than 0.1, the loss tangent and power factor are the same within experimental error.
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[5] The solution of the generalized bridge equations can be shown to be:

$$Y_1Y_3 - Y_2Y_4 = \frac{V_1 + V_{11}}{V_1 + V_{11} - 2V_{14}} (Y_1Y_2 - Y_{11}Y_3)$$

where Y_1, Y_2, Y_3, Y_4 are the admittances of the four arms of the bridge proper, Y_1 and Y_{11} are the admittances to ground of the two detector points of the bridge, V_1 and V_{11} are the potentials of the detector points with respect to the ground, and V_{14} is the potential of one of the source points with respect to ground. The right-hand side of the equation can be made equal to zero by making $V_1 = V_{11} = 0$, which is the object of the Wagner-grounded bridge technique. However, if the balance adjustments of the bridge proper depend appreciably on the values of the admittances in the Wagner ground and in the source, as is often the case for shielded bridges, it may be difficult to adjust V_1 and V_{11} to zero. This dependence can be materially decreased by the adjustment of either Y_1 or Y_{11} to make $Y_1Y_2 \approx Y_{11}Y_3$. Thus the proper adjustment of R_g in the present bridge arrangement decreases the dependence of the balance adjustments of the bridge proper on the Wagner ground and source admittances, and materially decreases the effort required to balance the bridge.

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APPLICATION OF RUBBER LATEX TO WOOLEN HOSIERY *

G. H. Piper

The application of rubber to textiles has made great progress within the last ten years, and the introduction of rubber latex with its high resistance to aging, which is of great importance where textile apparel is worn next to the skin, has virtually opened up a new field.

The sock has not altered greatly, and its greatest defect, the formation of holes at the toe and heel areas still remains. It was with the object of reinforcing these areas by impregnation with rubber latex that this research was commenced, resulting in the present process[1].

Briefly, the process is the application to the knitted sock, at the areas to be reinforced, of a rubber latex containing specified amounts of wetting and stabilizing agents so that the latex coagulates after penetration into the wool to a limited extent. The process is essentially an impregnation process, and the meshes between the threads remain open and free from rubber. The resulting hosiery is comfortable, and shows great resistance to the formation of holes.

In the development of the process, which occupied several years, numerous difficulties were encountered, not the least being the severe conditions to which the rubber is exposed. The warmth of the body, perspiration, laundry treatment and other factors necessitated a latex compounded to give high resistance to aging.

In the early experiments, a dilute latex of approximately 35 per cent dry rubber content, with an ammonia content of 1.1 per cent, was used, to facilitate penetration of the latex into the interstices of the wool threads and to prevent coagulation. The fabric was squeezed, and excess latex blocking the meshes of the fabric was removed by a blast of air through the area treated. The fabric was then dried and found to be strongly reinforced. With some types of woolen hosiery difficulty was experienced in getting satisfactory impregnation; with these it was found of advantage to work the fabric while in the latex to secure penetration. The ease of penetration depends to a considerable extent on the twist of the threads and the resulting distance between the fibres, and also on the presence of traces of oily substances left on the wool.

Although satisfactory reinforcement was obtained by this method, the results from the textile point of view could not be regarded as satisfactory, as the handle was greatly altered, and the large amount of rubber present in the knitwear gave a rubbery feeling when the sock was worn.

These difficulties were finally overcome my brushing or spraying a compounded latex in limited quantity onto the outside of the hosiery. The latex contains wetting and stabilizing agents, and its viscosity and coagulating rate are controlled so that the latex may soak into and impregnate the outer layer, yet coagulate before reaching the inner layer of knitwear. The inner layer of knitwear, next to the skin, is thus almost entirely free from rubber, and the full woolen feeling of the textile is retained. Wetting agents, such as sulfonated laurol, Vulcastab A or sodium cetyl sulfate and Lissapol, many of which are of

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the anionic soap class and also function as stabilizers, have been used in practice. The amount of wetting agent appears to depend on the type of woolen thread and degree of tightness or twist of the fibres, excess of the wetting agent resulting in the latex striking through to the inner layers of knitwear before it has time to coagulate. Experiments show that the time taken for latex to penetrate depends on the amount of wetting agent.

The use of a wetting agent has been found to be essential for the satisfactory treatment of woolen fibres by latex. Wool fibres in general are not readily wetted and scoured fibres, which usually have traces of absorbed fat acid, are similarly water-repellent. Rubber latex applied to such fibres shows little tendency to form an aqueous coating around the fibre, and does not readily penetrate the interstices of a woolen thread. By incorporating an adequate quantity of a wet-

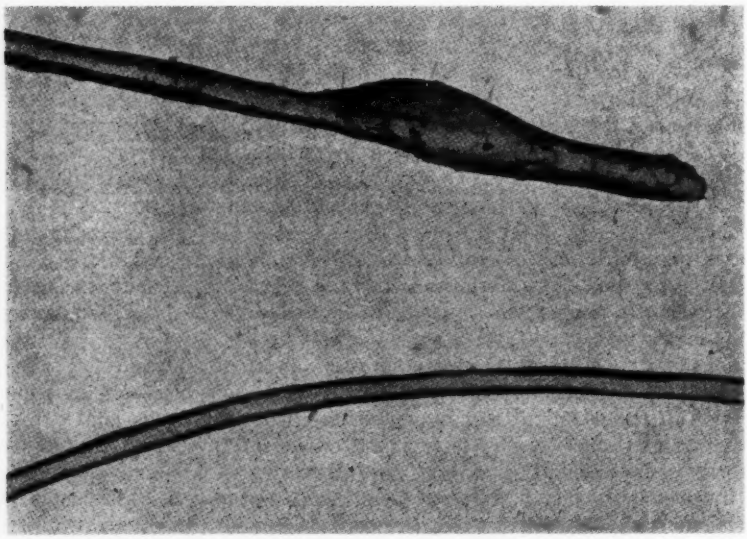

FIG. 1.—(Magnification, 80.)

ting agent, the latex is made to wet the fibres and, when dried, the fibre is covered with a thin coating of rubber. This coating is not readily observed, owing to the transparent nature of the dry rubber coating, but can be shown by using a rubber latex containing a dispersed pigment. Figure 1 is a photomicrograph, using a yellow filter of an undyed wool fibre which has been dipped in a latex mix of the type used in the process, to which some ball milled-heliomarine suspension has been added, and allowed to dry. The fibre was roughly washed and then examined; it showed a uniform blue coating, corresponding to the blue pigment dispersed in the rubber coating. The blob at the end of the fibre indicates a considerable thickness of latex rubber at this part. The lower fibre in the figure is untreated, and is included for comparison. The difference in opacity between the fibres was more evident by direct microscopic examination than in the microphotograph shown.

Microscopic examination shows also that the latex tends to congregate (presumably for capillary reasons) at the points of contact where fibres cross, and thus to cement them together at these points. The tensile strength of the thread,

which in the untreated state depends on the lengths of the wool fibres and the degree of twist, may thus be increased considerably.

An alternative method for impregnating wool with rubber was developed by the Wool Industry Research Association at about the same time. In this method a dilute positively charged latex, prepared by adding negative latex to a solution of a kationic soap such as cetyl pyridinium bromide, is used. This latex, which is stable for a few weeks and eventually flocculates, has the property of depositing rubber on yarn or fabrics, the bath being gradually exhausted. Advantages claimed are the convenience of an exhaustion process, and the avoidance of a rubber skin on the fabric. It is clear, however, that the formation of a skin can be avoided and satisfactory impregnation obtained by methods using negative latex.

A latex mix developed for the process, of the negatively charged type, is:

Rubber latex (60 per cent centrifuged)	50 g.
Vulcastab A (as paste)	1.35 g
Casein	0.6 g.
Soluble dyestuff	trace
Ammonia (0.880)	2.4 cc.
Water	16 cc.
Vulcanizing dispersion	1.96 g.

The vulcanizing dispersion has the composition:

Sulfur	1 part
Zinc oxide	1 part
Zinc diethyldithiocarbamate	0.75 part
Antioxidant	0.5 part

It was made by ball milling 50 parts of the above ingredients with 44 parts of water and 6 parts of Dispersol L for approximately 48 hours.

As the latex mix is used for impregnating a mass of textile fibres, it is essential that the vulcanizing dispersion should contain the particles in as finely divided condition as possible.

The mixture above ball-milled without foaming (casein tends to foam in the ball mill) and did not readily reaggregate. To avoid the latter, it is advantageous to use the dispersion soon after preparation.

The latex mix (41 per cent solids) contains 1 part of sulfur or zinc oxide per 100 parts of rubber, and an antioxidant is incorporated to assist the rubberized fabric to withstand the severe aging conditions. These latter include body temperature, perspiration, sunlight and repeated laundry washings.

In practice, the above mix is applied, preferably by brushing or spraying, onto the area to be reinforced, followed by a slight lateral stretching of the fabric to assist the latex to penetrate and clear the meshes of the fabric. The sock is dried naturally for a period, and then vulcanized for 45 minutes at 100° C. The structure of the latex impregnated area is shown in Figure 2, which is a photograph at a magnification of 35. A dyed latex mix of the above composition has been applied to a white piece of knitwear, the latter being also shown in the untreated state for comparison on the left of Figure 2.

After vulcanization, the treated areas are given a finishing treatment to eliminate any slight surface drag due to the rubber impregnating the outside threads. As latex coatings containing no fillers are practically transparent in thin films, the appearance of the outside of the treated areas is hardly altered from that of the original material. Where the latter is dark colored, however, a trace of soluble dyestuff is added to the latex to match the material.

On examination inside out, the finished hosiery shows no sign of the impregnated rubber, and has the usual woolen feeling. The treated areas at the toe and heel have, however, remarkably increased resistance to abrasion. The increase in durability was investigated by means of an apparatus consisting of a weighted scraper moved backwards and forwards over the fabric. The number of strokes necessary to wear through the fabric was counted.

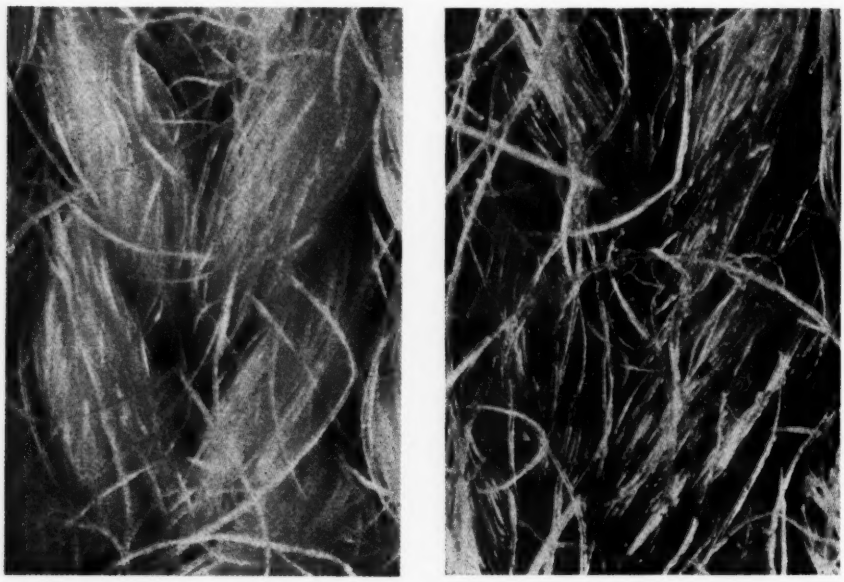

FIG. 2.

DURABILITY

(Determined by the Retail Trading Standards Association)

Untreated fabric ..... 8,300 Treated fabric 24,000

The increase in durability depends on the amount of rubber deposited in the fabric. In general the amount of rubber should be sufficient to cause adhesion at the points of contact of the wool fibres, but insufficient to fill the interstices between the fibres constituting the wool thread. Typical amounts of rubber for different types of sock are as follows:

	Weight of fabric per sq. cm.	Percentage by weight of rubber
Medium weight hosiery.....	0.026 g.	30
Heavy weight hosiery (army sock).....	0.06 g.	18 to 21

The increase in durability of the order of 3 to 5 times, measured experimentally and by actual wearing trials, can be understood by consideration of the nature of the wool threads and the stresses imposed during wear. The stresses are mainly of two types, first a tensile stress, and secondly an abrasive stress. Wool threads consist of short staple fibres twisted together, and their strength depends on the length of fibre and the degree of twist. They are also naturally weak in resisting abrasive forces, as the fibres are successively frayed out until the thread breaks. Tension is resisted by the interlocking of the

threads until, if the force is increased sufficiently, a point is reached at which the fibres slide past each other and breakage occurs. The tensile strength thus depends largely on the degree of twist and the length of the fibres. When lightly impregnated with latex, adjacent fibres are cemented together at points of contact, so slipping of the fibres past each other under tension no longer occurs, and the tensile strength and resistance are greatly increased. Experiments with larger fibres under conditions which can be observed more closely show that the increase in strength is limited by the weak adhesion of the dry rubber to the surface of the fibre.

The incorporation of a protein substance, such as casein, in the latex was found to increase greatly the adhesion to the fibre surface and to improve the tensile strength and resistance to abrasion. To test the resistance to abrasion, two mixes, one with and the other without casein were prepared. These contained approximately 30 per cent dry rubber content, and the former, 5 parts of casein per 100 parts rubber. The mixes were prepared from 100 cc. of latex (60 per cent centrifuged), 1.2 grams of Vulcastab-A paste, and 100 cc. of water. To the former mix, 3.0 grams of casein was added. The results of the tests are as follows:

Weight of impregnated thread per inch.....	0.004 g.	0.004 g.
Number of strokes for breakage.....	1040	580

Actually the mix used for the impregnation process contains 2 per cent casein on the dry rubber content. Increasing the percentage of casein stiffens the rubber and slightly stiffens the impregnated textile, but markedly increases the adhesion of the dried rubber to the surface on which it is deposited. Rubber films containing higher percentages of casein of the order of 15 parts to 100 parts of rubber show moderately high tensile strengths when dry but, when wetted and allowed to absorb water, exhibit an alarming fall in tensile strength which is not observed in the absence of casein. This fall is shown both by unvulcanized and vulcanized films of rubber. The fall in tensile strength is reflected in the ease with which the rubber can be rubbed out of the fabric when wet, and presumably arises from the presence of the water soluble casein. As the rubber impregnated fabric has to resist the effects of humidity while being worn and also in the laundry process, higher percentages of casein are undesirable. Treatment of the impregnated fabric with formaldehyde solution to render the casein insoluble prevents the large decrease in tensile strength on wetting and makes the use of such mixes possible.

The nature of the impregnation process with rubber latex may now be discussed in greater detail, with special reference to the impregnation of woolen fabrics. The use of a wetting and stabilizing agent is essential, and modern types of wetting agents, which include the sulfated fatty alcohols and their salts such as sodium cetyl sulfate (Vulcastab-A), sodium oleyl sulfate, sulfonated laurol (sodium lauryl sulfate), Gardinol, etc., have been found suitable. These substances, of the same type as turkey red oil (sulfated castor oil) usually consist of a long fatty chain coupled to a sulfonate group or a sulfate group, the latter group being strongly hydrophilic or attractive towards water molecules. They are classed as anionic soaps as they ionize in solution, giving a surface active anion with a negative charge. Thus, sodium lauryl sulfate gives:

$$C_{12}H_{25}\text{-}O\text{-}SO_3Na \longrightarrow C_{12}H_{25}\text{-}O\text{-}SO_3^- + Na^+$$

In the emulsification of oils with these soaps the soap is absorbed at the oil-water interface, the anion being orientated at the surface of the oil globule with

the fatty chain of the anion dissolved in the oil, whereas the strongly hydrophilic sulfate group is directed outwards into the water. It appears probable that, in the stabilization of latex with these soaps, there is a similar orientation of the soap at the boundary surface of the rubber particle, the fatty chain being directed inwards toward the rubber hydrocarbon and the hydrophilic sulfate group outwards into the serum. The latex is thus stabilized, both by the increased negative charge conferred and by the protective coating of adsorbed soap and attracted water molecules. A similar state probably exists, with some modification, when a protein substance is present in addition to the anionic soap. It has been shown by Twiss[2] that the isoelectric point of natural latex, which occurs at p_H4.5 and is characteristic of the naturally occurring film of adsorbed protein, is shifted to much lower values in the presence of anionic soaps. Nekal, a complex sulfonic acid, alters it so that it is not even reached at p_H2. It is concluded that the protein sheath round the latex particles is easily displaced by these sulfated compounds, which act as stabilizers.

The latex mix found suitable for the process contains 0.37 per cent of the wetting agent (sodium cetyl sulfate). Surface tension measurements on aqueous solutions of similar wetting agents, such as Igepon, show that 0.1 to 0.2 per cent effectively reduces the surface tension. Increased concentrations have little further effect[3]. When applied to the knitted fabric the latex mix soaks into the threads at an appreciable rate, depending on the amount of wetting agent. As the latex is applied in limited amount it may completely disappear, under suitable conditions, into the interstices of the fabric. The rate at which the latex soaks through diminishes rapidly with time after the initial application, and in about ten minutes the latex has coagulated on the fibres. There is evidence that this coagulation does not result merely from the loss of ammonia and loss of water by evaporation. For if the latex is previously deammoniated by standing some time in the open and applied to the woolen fabric, which is then placed in an atmosphere of 100 per cent humidity so as to avoid loss of water by evaporation, it is found after some time that the latex has coagulated round the fibres. The impregnated fabric may then be rinsed in water without losing rubber. As coagulation in this case does not result from loss of ammonia or water from the latex, and the wool had a normal p_H 7 to 7.5, it appears probable that the process of coagulation around the fibres arises from the gradual adsorption of the latex stabilizer on the wool fibres and the simultaneous loss of stabilizer from the boundary surface of the rubber particles until the latter are able to aggregate.

The sorption of the wetting agent or stabilizer by the wool fibre is clearly an important factor in the impregnation of woolen textiles by rubber latex, and will now be discussed in the light of the theoretical and experimental evidence available. The structure of the wool fibre has been studied by Speakman[4], and others on the basis of the chemical and x-ray evidence.

Apart from the scaly covering of the wool fibre, it is believed that the wool fibre consists of micelles of lamina shape, arranged with their long axes parallel to the fibre axis. The micelles are flat, have a greater length than their breadth, and probably lie tangentially to circles described around the fibre axis. The micelles consist of long polypeptide chains or ladders superimposed on one another, and these ladders or chains are believed to be bridged by rungs or linkages of two types, first salt linkages formed by the interaction between carboxyl and amine groups, and secondly cystine or disulfide linkages.

The wool fibre swells in water to the extent of approximately 17 per cent along the fibre diameter, and the elastic properties are modified. The energy

required to extend the fibre by 30 per cent is decreased to about one-quarter, and by measuring this energy when the fibre is immersed in alcohols of increasing molecular weight, it is concluded that alcohols of greater size than *n*-propyl alcohol are unable to penetrate into the fibre. The interstices in the dry wool fibre are therefore given a diameter of approximately 6 A.U. When swollen with water, however, alcohols up to octyl alcohol are able to penetrate the fibre, and it is thus concluded that in the swollen fibre the interstices have a diameter of the order 41 A.U. This large increase in diameter on swelling, in conjunction with the comparatively small increase in the fibre diameter, affords support for the view that the water is penetrating into the interstices between the micelles and not to any extent into the micelles themselves, a view supported by the x-ray evidence as the x-ray pattern is unaffected by the swelling.

In acid solutions, especially with weak acids of p_H lower than 5, a different phenomenon takes place; the swelling is larger and the x-ray pattern is altered, becoming characteristic of amorphous structures. It is believed that the water enters the micelles themselves, being enabled to do this by the acid severing the salt linkages between adjacent polypeptide chains and thus reducing the cohesion between the latter so that the micelles are free to expand. The action of the acid on the salt linkages consists of combination of hydrogen ion with the carboxyl group of the salt linkage, and association of the liberated $-NH_3^+$ group attached to the wool structure with the anion of the acid.

Sulfated and sulfonated wetting agents have some similarity to the acid dyestuffs used for wool dyeing. The majority of the latter have a sulfonate group, and are used in the form of the sodium salt, the dye bath being used hot and acidified. A considerable amount of work has been done on the dyeing process, and it seems probable that sorption of the sulfated wetting agents by wool is analogous in many respects to sorption of acid dyestuffs, particularly in acid solutions.

In the process of acid dyeing, it is believed that the acid functions as described above, allowing the micelles to swell and rendering them accessible to dye molecules. Recent work, however, suggests that the accessibility depends on the size of the dyestuff molecule, for large dyestuff molecules do not penetrate the micelles. It has been found that wool does not combine with acid above p_H 5 or with alkali below p_H 7, *i.e.*, it has an isoelectric region between p_H 5 and p_H 7. Through breakage of the salt linkages, at a given hydrogen ion concentration in an acid dyebath there will be a certain number of $R-NH_3^+$ groups available for combination with the negatively charged anions of the inorganic acid and dye, R representing the wool structure linked to the NH_3^+ group. In the first stage the inorganic acid anions in association with $R-NH_3^+$ groups preponderate, but subsequent diffusion of dye anions results in displacement of the inorganic acid anions, and the fibre is dyed.

This theory, which regards the process of dyeing as a process involving salt formation between the color acid and the protein, explains the observed facts. Elöd[6] applies on this basis the Donnan theory of membrane equilibria to the system, and shows that the increasing amount of dyestuff absorbed as the p_H is lowered, and the occurrence of a maximum, is explained, as well as the levelling effect of neutral salts. This concurrence does not necessarily prove, however, that the dyestuff is actually present inside the micelle itself.

The sorption of some sulfated wetting agents by wool has been investigated by Neville and Jeanson[3], who showed that at p_H 6 there was a moderate sorption of wetting agent, which increased rapidly as the p_H was reduced below 5.

In the process described for the impregnation of wool with latex, the latter with wetting agent is used alkaline, with a p_H approximately 9.5. It is thus improbable that at this p_H the wetting agent becomes sorbed inside the wool micelle. As little experimental work was available on the sorption of sulfated wetting agents at p_H values other than acid, it was decided to investigate the sorption of Vulcastab-A (sodium cetyl sulfate), the wetting agent used in the process. Owing to the complexity, it has not so far been possible to make a complete study of the system, and it is intended to publish the completed results later.

The method used was to treat 10 grams of the wool with 100 cc. of sodium cetyl sulfate solution, agitate at intervals and, when sorption had taken place, a measured volume of the solution was removed by a pipette and the amount of solid present determined by careful evaporation. The wool was in the form of undyed serge, and was previously extracted with hot alcohol and then acetone. p_H values were determined at the conclusion of the experiment with a colorimetric indicator, and are to be regarded as only approximate, in view of the presence of sulfated wetting agents.

Wool was treated at 24° and p_H 8 with two solutions of sodium cetyl sulfate. After 20 hours, the sorption values calculated, per 100 grams of wool, were 0.26 gram at a concentration of 0.094 per cent and 0.68 gram at a concentration 0.29 per cent. As it was uncertain whether sorption equilibrium was attained, the experiment was repeated, wool being treated with 0.358 per cent sodium cetyl sulfate solution. After 15 minutes, 1, 2, and 20 hours, respectively, the sorption values recorded were zero, 0.19, 0.34 and 0.68, respectively, the concentration at 20 hours being 0.29 per cent. Sodium cetyl sulfate was then withdrawn from the system by replacing part of the solution with water and, after 20 hours, the sorption was 0.82, the concentration then being 0.094 per cent. It is thus clear that sorption equilibrium is not attained at this temperature under these conditions, and full elucidation of the sorption process is difficult. From the slow rate of sorption, which indicates a slow diffusion or solution process, it is clear that sorption is not a simple adsorption of molecules on the outer surface of the fibre. The process may be either slow diffusion of the molecules into the micelles or, alternatively, slow diffusion of the molecules between the micelles, *i.e.*, along the interstices in the fibre, and their adsorption on the internal surface. From evidence on the swelling of wool fibres in water, it is unlikely that the former process occurs under neutral conditions, and it is believed that the latter mechanism is the correct one, *i.e.*, adsorption of anions of the wetting agent in the interstices between the micelles. The slow rate of adsorption from the start is consistent with slow diffusion of the anions down the narrow cracks between the micelles and the large internal surface offered by these cracks. Further, the rate of sorption at p_H 10 was almost identical with the rate at p_H 8. It is clear that sorption under neutral conditions is not sorption of anions into the micelles and their combination was positively charged NH_3—groups (even assuming these are present) attached to the side chain of the polypeptide chains.

It is more probable that adsorption is one of anions on the neutral surface, the adsorption forces being of the weak van der Waals or physical type. Sulfated wetting agents ($R\text{-}O\text{-}SO_3Na$) possess a strongly lyophilic sulfate group attached to a long hydrocarbon chain (R) which is not wetted by water. Owing to the strong intramolecular attraction between water molecules, and the presence of the hydrocarbon chain to keep them apart, there is a strong tendency for the hydrocarbon chain to be squeezed out of the water. This may take

place by adsorption of the hydrocarbon chain on a surface. This type of adsorption may occur on comparatively inert surfaces, and it is unnecessary to assume large molecular forces between surface molecules and adsorbed chains.

A further type of adsorption of sulfated wetting agent in protein fibres is a possibility in the isoelectric region. The salt linkage is a link of an ionic type, consisting of a negatively charged carboxyl group and a positively charged NH_3 group. It is clear that this link will give rise to a large electrical field in the vicinity, and that the positively charged group will exert an attraction for an anion in solution such as the sulfate group of a wetting agent. The electrovalency of a charged atom is not completely saturated by its association with a single atom of opposite sign, as is shown in the crystal lattice of sodium chloride, where each sodium ion is surrounded by six symmetrically placed chlorine ions. Hence a strong attraction for the anion will be exerted by the positively charged group of the salt linkage, without it being necessary to assume that the latter is broken. These salt linkages will be exposed on one surface of the wool micelle, and thus adsorption on this surface of an ionic type is possible in the isoelectric region.

In this latter type of adsorption, the sulfate group is attracted to the surface, whereas in the previous type discussed the hydrocarbon chain end is adsorbed on the surface.

Further information on the adsorption process is obtained by measurements at higher temperatures. At 38° C and p_H 8, the sorption value at 20 hours was 1.98 grams. This higher value might be anticipated from a more rapid sorption velocity. However, on cooling the system to room temperature, sorption fell from 1.98 (concentration 0.16 per cent) to 1.59 (concentration 0.21), after 20 hours. As the sorbed molecules are now leaving the fibre, it is clear that the system has at one point passed through the equilibrium stage and that the equilibrium adsorption at room temperature is actually less than at higher temperatures. In the ordinary way it might be deduced, applying Le Chatelier's Law, that the adsorption process is endothermic. However, the net heat change in the system includes not only that due to adsorption, but also that due to change in equilibrium with temperature of the aqueous phase. It has been established that the long chain ions of these wetting agents tend to aggregate in solution to form colloidal micelles with an electrical charge, the solution containing these ionic micelles in equilibrium with the simple ions; this aggregation becomes marked above a certain critical concentration. If, as seem probable, the heat effect accompanying changes in this latter equilibrium is small, it follows that the process of adsorption is endothermic. This process of adsorption involves displacement of adsorbed water molecules from the surface, which is an endothermic effect, and it is clear that adsorption of the sulfated wetting agent itself on wool at this p_H involves only weak molecular forces.

The latex mix used in the process contains 0.37 per cent of wetting agent (sodium cetyl sulfate), the latter being present partly as an adsorbed layer on the latex particles and partly in the serum. In contact with the wool, adsorption of the wetting agent takes place. Calculation shows that adsorption is great enough to reduce considerably the free concentration in the latex and thus to reduce the stability of the latex. As the latex penetrates into the fabric, ammonia is lost, and stabilizer increasingly removed by adsorption on the fibres. Both effects decrease the negative charge on the latex particles, and the latex ultimately thickens and coagulates around the fibres. The type of coagulation obtained is important for correct functioning, and the coagulation time, the

relevant factor, depends on the proportions of ammonia and stabilizer, and especially their relative proportions.

A further function of the wetting agent is to secure penetration of the latex into the interstices on the fibre surface. As mentioned above, the adhesion of a dry rubber film to the fibre surface is not great, and it is probable that penetration of the latex around the irregularities on the fibre surface helps materially to key the rubber coating to the fibre surface.

A factor opposing wetting of knitted woolen hosiery is the presence of traces of oil derived from the knitting oil added to facilitate the knitting process. This oil consists mainly or entirely of oleic acid, and is usually removed by scouring with a soda bath. The last trace of oil, of the order of 0.2 to 0.3 per cent, is difficult to remove, and possibly exists as an adsorbed film. Where traces of oil exist, the alcohol chain part of the anion of the wetting agent dissolves in the oil and the hydrophilic sulfate or sulfonate group overcomes the water-repellent nature of the oil. Difficulties in production have arisen during the war, as a result of the use of inferior oil substitutes not readily scoured from the wool. Owing to variation in the amount of residual oil left on the wool, it may be necessary to alter the concentration of wetting agent in the latex. The wetting of wool is also influenced by its previous history. The chlorinating process for making wool unshrinkable, involving treatment with dry chlorine or with chlorine in solution, has a large influence, and shifts the isoelectric point of the wool (as measured by the zeta potential) to lower p_H values.

A new field, not so far investigated, has been opened by the recent development of synthetic wool fibres. These fibres are mainly protein fibres derived from casein, soya bean or other sources. They are not completely satisfactory as regards tensile strength and other properties, and it is possible that their successful utilization in the future may depend on their treatment with rubber latex.

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DUNLOP FATIGUE TEST FOR RUBBER COMPOUNDS *

V. E. Gough and D. Parkinson

INTRODUCTION

This paper considers the effects produced inside a block of rubber subjected to repeated cycles of stress. Other types of fatigue, such as flex cracking or the phenomenon recently referred to by Cadwell, Merrill, Sloman and Yost[1] as static fatigue, are not discussed.

The fatigue test which will be described in the following pages has been used for a number of years in the Dunlop Rubber Company's laboratories. The test machine, like others which have been described by Martens[2], Vogt[3], Abbott[4], Depew and Snyder[5], Cooper[6], Havenhill and Macbride[7], Havenhill[8], Lessig[9], and Roelig[10], can be used for assessing heat development, the failure produced in the test-piece being then of the "blow-out" type, or it can be used to produce breakdown in specimens which have been stressed for prolonged periods at a moderately high, although steady temperature. The failure may then be considered to be one of fatigue and not one of thermal decomposition, although, as will be shown, the heating effect is one of the most important factors operating to produce failure.

Among the test machines referred to above, the one described by Depew and Snyder[5] is similar to the Dunlop machine, an early form of which was already in use for the purpose of evaluating heat generation in solid tire compounds when Depew and Snyder's paper was published in 1929. The present improved machine and technique are the result of several years of subsequent development work.

The stressing conditions of the machine, which produce direct compression, are as simple as possible and give results which vary less and are more easily interpreted than those obtained when they are more complex, as, for example, when they introduce shear in addition to compression.

DESCRIPTION OF MACHINE AND PARTS

Figures 1, 2 and 3 show the type of machine employed for the test. It is an ordinary belt-driven power press of the usual slider-crank mechanism, arranged so that the tool A, as it reciprocates, deflects and releases the rubber block S. The two machines in use have an adjustable stroke of 1 to 3 inches, and normal tests are carried out with the maximum stroke or throw. These machines are provided with independent motor drive, the motors fitted being variable speed one-half horse power, d.c., with a machine speed range from 150 to 300 r.p.m. The tool A has a fibre insert so that the heat of the sample under test is not conducted away.

The test-piece S is mounted on a table F, which is prevented by means of a stop from rotating while the adjusting screw E, which supports the table from the top of the piston D, is being turned to adjust the table height. The screw E is of fine pitch (approximately 2 mm.), of sturdy construction, and can be

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 17, No. 4, pages 168-239, December 1941.

locked in any desired position by means of the knurled locking nut L. "Tommy bar" holes are provided in both the screw E and the nut L to facilitate adjustments under running conditions.

The actual mounting of the specimen is effected by clamping its base to a fibre disc by means of a fibre ring and the whole held to the steel head or table F

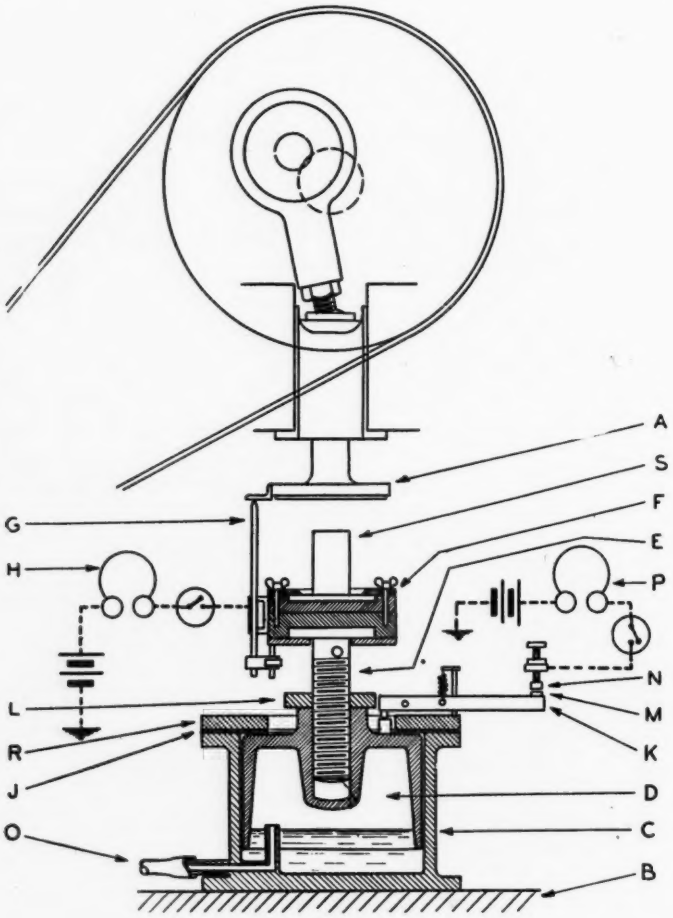


FIG. 1.—Dunlop fatigue testing machine.

by means of four wing-bolts. The underside of the block is also cemented to the fibre with plain rubber naphtha solution. As in the case of the tool, fibre is used so that the generated heat is not conducted away to any appreciable extent, as all surfaces which come into contact with the rubber have low conductivity.

The deflection and free height of the block are measured by means of a scale and vernier G, marked to read to 0.02 mm. when used together. Readings are taken by raising the scale to touch a steel plate on the underside of the tool, fine adjustment being obtained with the screw. The correct position of the scale

is found by the use of the telephones H. The scale is raised until a click is heard, indicating that the circuit has been completed as the scale touches the tool A.

The load measuring device is mounted on the platform B of the main frame of the machine. This apparatus consists of a cast iron cylinder C, into which

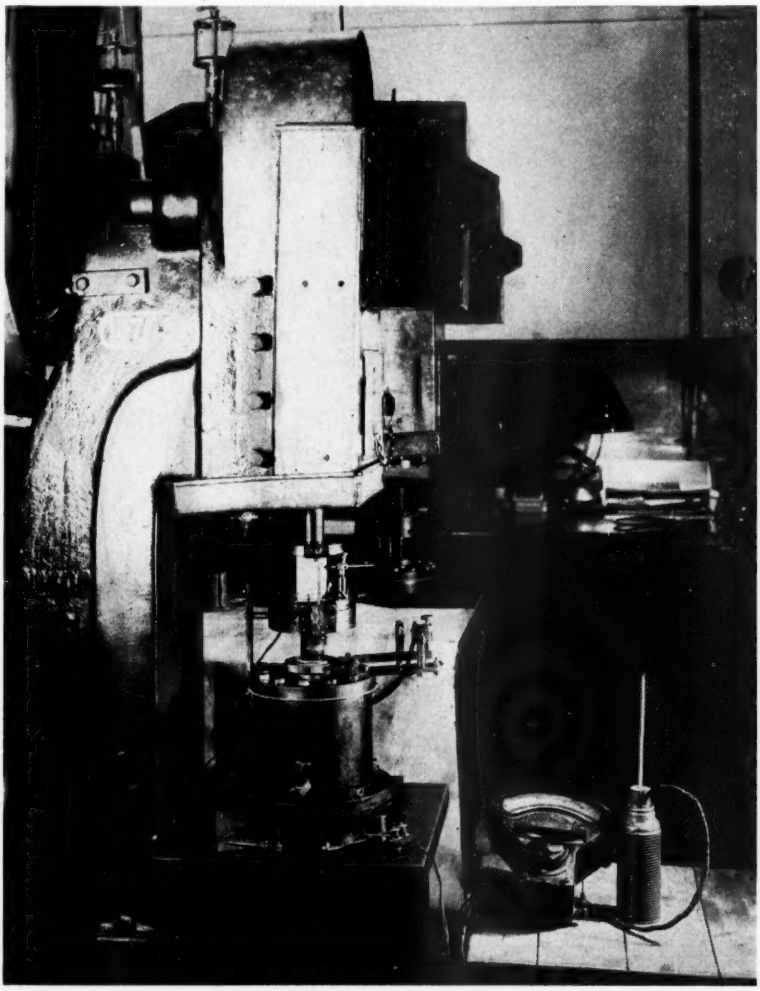


FIG. 2.

a plain steel piston D fits. The area of the piston which is operated on by the compressed air is 25 square inches. The piston has no rings or grooves, and air leakage is prevented by the use of castor oil, which also serves to lubricate the piston when in motion. A retaining ring or flange R prevents the piston from leaving the cylinder. Between this ring and the piston top a washer or layer J of composition packing ($\frac{1}{16}$ inch thick) is interposed. The bolts holding R in place serve to position this washer. This composition packing must have the fol-

lowing qualities for successful operation of the machine: (1) it must be hard, even when surrounded by oil which has leaked past the piston; (2) it must be oilproof to as great a degree as is possible; and (3) it should provide a good flat and air-tight seating to the top of the piston when under working conditions. The material used is known as Permanite.

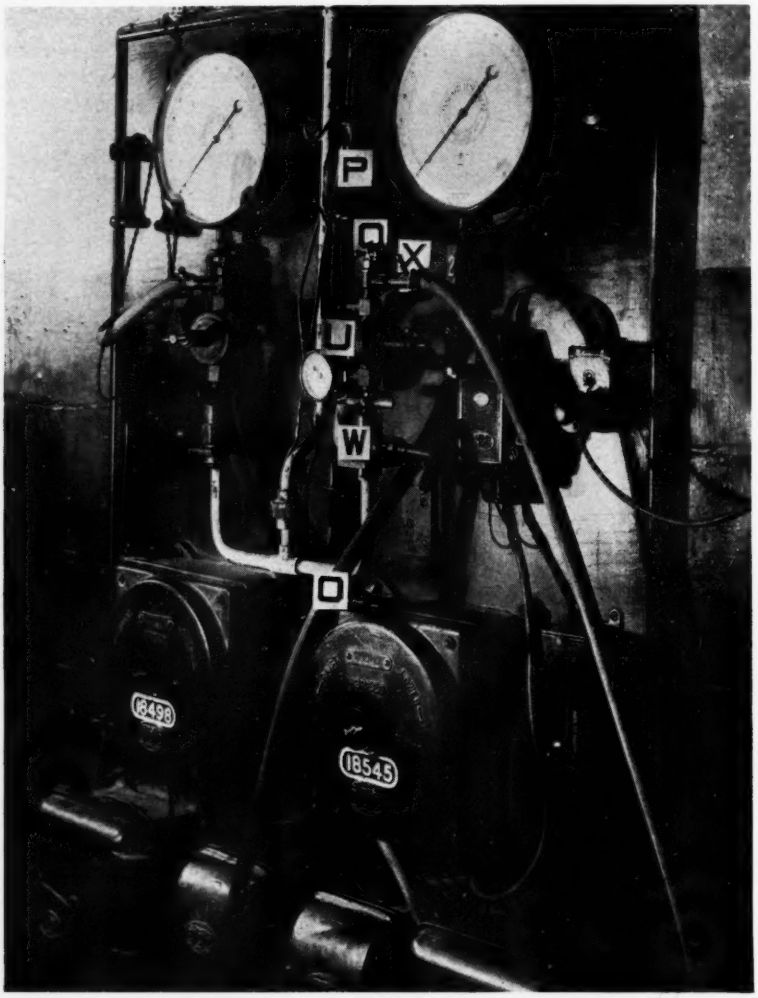


FIG. 3.—Control panel for two machines.

Mounted at K on the cylinder C is an electric contact, which is arranged so that the motion of the piston moves a lever M and so opens and closes the contacts M and N in an electric circuit, which also includes a telephone P. The lever magnifies the piston movement in the ratio 8 to 1. The upper contact N, which is the stationary one, is adjustable by means of a screw, and is set so that the gap is between 0.025 and 0.027 inch by means of a feeler-gauge. This

corresponds to a piston movement of approximately 0.003 inch at the instant when the load is measured. This value was chosen after a careful analysis of the dynamics of the system (see Appendix A).

It follows that the contacts close as the piston passes a point 0.003 inch below its normal position, and open as it passes the same point on the return motion. The cylinder C is supplied with compressed air through a reducing valve U (see Figure 3) from the mains. The air pressure is normally 5 to 10 lb. per sq. in. above the value which just allows the piston to move.

METHOD OF MAKING MEASUREMENTS

Free-Height of Test-Piece.—The measurement of the free height is made out when the machine is not running. The top of the block is lightly dusted with French chalk, and a piece of tracing cloth of known thickness is inserted between the block and tool A. The tool is lowered on to a small screw-jack (placed to one side of the block as shown in Figure 2), which is then adjusted so that the tracing cloth can be moved with but slight resistance.

The scale is then raised to touch tool A, contact being indicated by a click in the telephones. To obtain the true position of the top of the block with respect to the zero of the scale and vernier, the known thickness of the tracing cloth is subtracted from the scale reading, and to obtain the true free height, a further constant (due to the use of an arbitrary zero) has to be added to this value.

Deflected Height.—This measurement is made when the machine is running by gradually raising the scale until clicks are heard in the phones indicating that the tool touches the scale at the lower end of its stroke at each revolution of the machine. The value obtained is the deflected height above the scale zero, and the difference between this reading and the free height above the scale zero gives the actual deflection of the specimen.

Maximum Load.—To obtain the magnitude of the load acting on the block at the point of its maximum deflection at any time during a test, the air pressure in cylinder C which just allows a known movement of piston D to occur (while the machine is running) is required. Before a pressure reading is taken, the gap M N is checked to ensure that it is between 0.025 and 0.027 inch. The telephone circuit is closed and the main air valve W closed. The air in cylinder C (Figure 1) is then released by means of the release valve X (Figure 3). When the piston is moving, the valve Q is shut and the main air valve W opened; the air is then allowed to return into the cylinder by adjusting valve Q. This is repeated with the air released and opened slowly, and the load at which the telephone clicks cease is estimated to 0.1 lb. per sq. in. The readings should not differ by more than 0.2 lb. per sq. in. with rising and falling air pressure; if they do, the air flow is too rapid and must be reduced. The first piston movement is ignored in the estimation of load because surface tension and similar effects due to the oil between the piston and washer introduce errors which are absent in the succeeding readings.

A correction is applied to the pressure obtained above to obtain the true effective pressure which, when multiplied by the area of the piston, gives the true maximum load on the block when running under normal conditions, *i.e.*, with the piston stationary or, more accurately, with the air pressure 5 to 10 lbs per sq. in. above that which just allows the piston and washer to separate. The value and method of determination of this correction are discussed later.

TEMPERATURE AT CENTRE OF BLOCK.—This is measured by means of a thermocouple when the machinery is stationary. The thermojunction is made from a hypodermic needle (1 mm. × 40 mm.) with a constantin wire inside and silver-soldered at the tip, which is then rounded off a blunt point. The meter used gives a full-scale deflection for 8 millivolts, and has a resistance of 100 ohms. A series resistance has to be inserted in the circuit when temperatures at the higher end of the normal range are encountered. The cold couple and room temperature thermometers are calibrated to 0.1° C to obtain temperatures to 0.5 C with accuracy. The cold couple is in a thermos flask (Figure 2).

By means of a sharply pointed wire (15 S.W.G.), inserted at one-half the height, a hole is made which passes to the centre of the block. When the temperature is being taken, the blunt thermojunction is inserted in the same hole each time.

MACHINE SPEED.—The total number of blows during a test is recorded by a counter.

A stroboscope, consisting of a graduated circular disc mounted on the crankshaft of the machine and illuminated by a neon lamp flashing 100 times per second on the alternating current mains (which are frequency-controlled), is used to obtain the machine speed at any instant. The graduations on the disc depend on the range of speed required, those in general use being made for the range 176 to 194 r.p.m., and having rings with the following numbers of equal graduations: 31, 94, 95, 32, 97, 98, 33, 100, 101, 34 in the order stated. The speed at which each of the rings would appear stationary is calculated on the basis that the angular spacing of one large or three small divisions is equal to the angle moved in 0.01 second. The machine speed is that corresponding to the ring which appears stationary, and if no ring is stationary, then the speed is intermediate in value between the two adjacent rings which appear to revolve in opposite directions, and is taken as the mean of the values corresponding to those two rings.

LOAD MEASURING DEVICE

The apparently obvious statement that the maximum load on the block is equal to the air pressure to prevent movement multiplied by the piston area is not strictly true. In the first place the piston is never quite at rest while the machine is running, as it can be shown by a microscope that the piston has a movement of the order of a few ten-thousandths of an inch under normal running conditions. Also at the instant at which the pressure is measured, the movement of the piston is three-thousandths of an inch. Considerations discussed in Appendix A indicate the necessity for this movement.

There are two ways of looking at the problem: (1) the change in air pressure modifies the spring factor of the whole system until the movement under a given load (due to the tool compressing the block) attains a predetermined value, and (2) the air pressure requires a correction to be added to allow for the inertia and damping of the piston.

Both ways lead to the same result, but the first is more convenient from the point of view of the mathematical study of the problem, whereas the second is the more convenient for practical application. Both aspects are considered in the appendix. Because of the use of an air cylinder, the correction to be added is small compared with the value measured, and can be made with a sufficient degree of accuracy to warrant its inclusion. If a helical steel spring had been used, a long spring would be required to keep the correction at such a low

value. It should be noted that the maximum load under normal running conditions is of importance, and not the maximum load at the moment of load measurement.

It is shown in Appendix A that, provided the contact gap is between 0.025 and 0.027 inch, the correction is 1.0 lb. per sq. in. to be subtracted from the observed gauge reading to get the maximum load operating on the block while the piston is at rest for blocks and tests within the following range: speed 180 to 192 r.p.m., work input 0.45 to 0.55 joules per cc., pressure gauge 40 to 60 lbs. per sq. in., deflected height 35 to 40 mm., room temperature 20° C, provided that other factors, such as oil levels and pipe lengths, remain as on the existing machines.

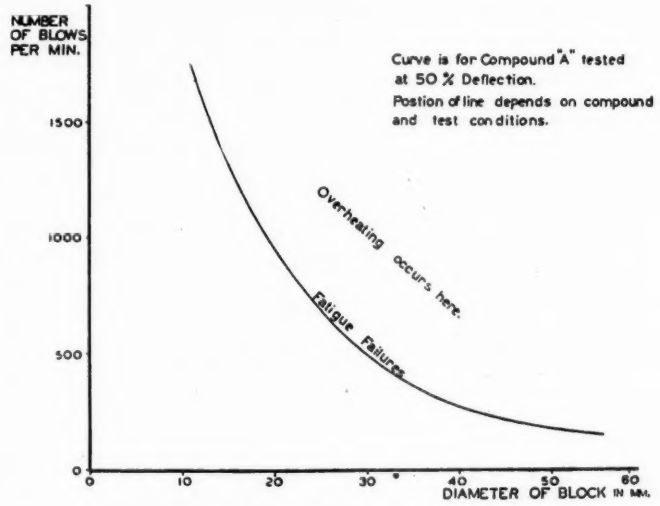


FIG. 4.—Approximate relationship between speed and block size to obtain similar failures.

BLOCK CONSTRUCTION

Blocks are made by rolling warm rubber about 3 mm. thick straight from the calender, into a cylinder of the required diameter, which is then trimmed to length. It is inserted into a mould, and a disc of rubber is laid in the recess in the mould to form the base. The moulds are stacked in the autoclave during cure, with the block axis vertical, and arranged so that flat steel plates between them act as end plates to each mould. Hydraulic pressure is applied along this axis.

The cures require long rises, owing to the size of the mould and block, a convenient rate of rise being 1 lb. of steam pressure per minute.

CONDITIONS OF TEST

The block dimensions, speed of test, load and deflection, running temperature and type of failure are interdependent, as is illustrated by Figures 4, 5 and 6.

Figure 4 shows how the type of failure is related to speed and block size. Figure 5 shows the effect of speed on the rate of temperature rise for various

sample sizes. Figure 6 shows that the temperature at failure falls as the life increases. These curves relate to a tire-carcass type of compound, subsequently referred to as compound A, which contains 50 per cent of zinc oxide by weight

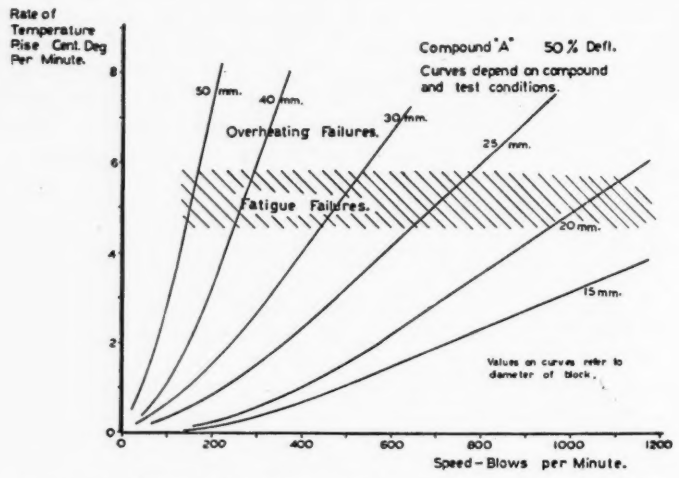


FIG. 5.—Approximate rate of temperature rise with various block diameters and test speeds.

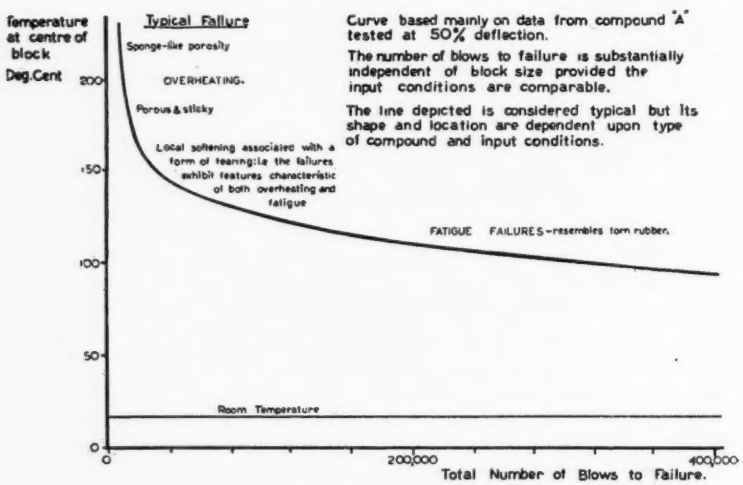

Temperature at centre of block Deg.Cent
Typical Failure
Sponge-like porosity
OVERHEATING.
Porous & sticky
Local softening associated with a form of tearing; the failures exhibit features characteristic of both overheating and fatigue
Curve based mainly on data from compound "A" tested at 50% deflection.
The number of blows to failure is substantially independent of block size provided the input conditions are comparable.
The line depicted is considered typical but its shape and location are dependent upon type of compound and input conditions.
FATIGUE FAILURES - resembles torn rubber.
Room Temperature
0
50
100
150
200
0
200,000
400,000
Total Number of Blows to Failure.

FIG. 6.—Approximate relation between temperature and number of blows to produce a failure internally.

on the rubber, is accelerated by mercaptobenzothiazole, and contains enough stearic acid to activate the accelerator, but no other softener.

BLOCK DIMENSIONS.—The size and shape of the test-pieces were chosen as the result of a number of tests on compound A under varying conditions. The principal factors which had to be considered were: (1) the conditions of test must be such as to produce failure of the rubber; (2) the failure should be pro-

duced in a reasonable time, say in one or two days; (3) the running temperature should be within certain limits, and (4) the ratio of height to diameter of block must be as great as possible without buckling. This is to minimize the effect of the frictional restraint of the transverse increase of size set up by the compressing platens, and so to ensure that the bulk of the block is in pure compression. Also it ensures that the main heat flow is radial rather than axial, and thus minimizes the effect of heat conductivity of the fibre block holder, etc.

The sample finally chosen has a circular section of 2 inch diameter, and 3 inches high, including a base 3.5 inches in diameter, and 0.25 inch thick, the purpose of which is for holding the block in position on the machine. The machine speed used for standard testing is 187.5 r.p.m., *i.e.*, the speed corresponding to the 32 dot ring on the stroboscope.

Running Temperature.—The temperature developed in the interior of the block during running is one of the most important factors producing failure of the rubber. It was found that if the temperature rose above a certain value, which was usually between 130° C and 150° C in carcass compounds, but higher than 180° C in pneumatic tread stock, the tendency was for the temperature to continue to rise, and the rubber failed from overheating after a short life.

This phenomenon is probably connected with the temperature of maximum resilience (or minimum hysteresis) of the rubber. Once the block is running at a temperature higher than that of maximum resilience, there is a fall in resilience with each increment of temperature, with consequent increase in the rate at which the heat is developed in the rubber.

On the other hand it was found that running temperatures much below 100° C resulted in excessively long lives before failure of the rubber. The testing conditions were, therefore, arranged so that a good quality casing or cushion compound would run between the limits of 100° and 130° C. Under severe road conditions, temperatures in the interior of giant covers sometimes exceed 100° C.

Load and Deflection.—The test can be operated under any of the following conditions: (1) Constant load, (2) constant percentage deflection, (3) constant work (*i.e.*, constant elastic energy input), or (4) some function of (1), (2) and (3).

The conditions used depend to some extent on the type of compound to be tested. Solid tire stocks, for instance, are naturally compared under conditions of constant load. It is less easy to fix conditions for pneumatic tire compounds, since the conditions of loading are not definitely known. It was decided to subject cushion and carcass compounds to constant work conditions for the following reasons:

(*a*) *Under constant load* a low-modulus or soft compound would receive a higher deflection than a high modulus or hard compound, and hence would receive a greater energy input. If the energy lost and hence the heat generated were the same proportion of the input energy in the two cases, then the temperature of the low-modulus compound would be the higher, with consequent earlier failure.

(b) *Under constant percentage deflection* a low-modulus compound would receive a lower load than a high-modulus compound, with consequent lower work input, etc.

(*c*) *Under constant work* the energy lost per cycle should, for the same power loss and thermal diffusivity, be independent of the modulus of the compound.

METHOD OF OBTAINING CONSTANT WORK

Originally the method of approximating to constant work (or energy input) was to maintain the product of load and deformation constant. This was obviously only a first approximation, but reference to the available literature did not reveal a more suitable basis for computation. In view of this, the relationships of the load to the deflection for rubber cylinders of various sizes and compounds, ranging from soft carcass compounds to hard solid tire treads, were investigated from both a static and dynamic standpoint.

Relationships Obtained from Static Tests.—The following results were found to be true up to approximately 55 per cent deflection (provided $H > D$) on static test made on a Buckton Universal testing machine.

Let Δ = fractional deflection of a block on its height
H = original height
h = deflected height
D = original diameter
d = deflected diameter
E = modulus below critical deflection (these terms are explained later)
L = actual load on block

(*a*) *Relation between diameter and height.*

$$\frac{d}{D} = \left(\frac{h}{H}\right)^{-0.59}$$

This applies to all block sizes and compounds (see Figure 7.)

(*b*) *Relation between load and deflected area.*—Below the critical deflection (approximately 55 per cent) $\frac{4L}{\pi d^2} = E\Delta$, where E is independent of the block dimensions, and has a characteristic value for each compound (see Figure 8).

At some point the load deviates from this law and increases more rapidly. This point is defined as the critical deflection. It depends on the compound and dimensions of the test-piece and, in general, is above normal operating conditions of the present test. The relations of the load to the deflection above the critical deflection have not been fully investigated.

(*c*) *Shape of Block under load* ($H < D$).—Under compression, blocks which are initially cylindrical do not become barrel-shaped, as is sometimes supposed, but assume a form which may be described as cylindrical with curved endcaps due to the friction between the block ends and loading plates. The height of the cap is approximately constant, of the order of 0.2 d. As the load increases, the cylindrical part decreases in length until at a certain point the end caps merge into each other; this point appears to coincide closely with the critical deflection. This explains the deviation from the original curve, as then the whole of the rubber is under restraint, due to the friction of the loading plates. It can be shown from conditions of symmetry that the compressive stress in the parallel part of the block is uniform (see Appendix C). In the authors' opinion, the fact that most other workers use blocks where $H < D$ (for practical and other reasons) prevents them from obtaining the relations given above as the critical deflection is low and is in the normal deflection range. This necessitates the use of a shape factor. It follows from present work that if a shape factor is necessary to explain the results of tests on compression cylinders, then the stress in the cylinders is not pure compression but is complex, and involves shears.

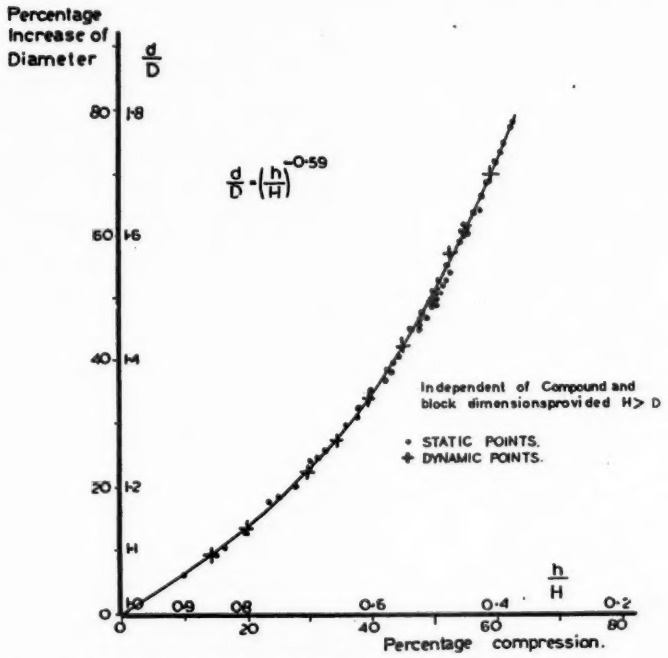


FIG. 7.—Relation between diameter and height of cylindrical blocks under compression.

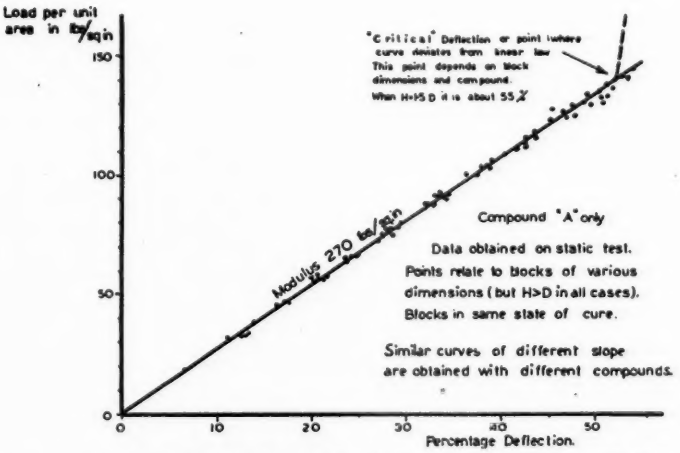

Load per unit area in lbs/sq in
150
100
50
0
10
20
30
40
50
Percentage Deflection.
"Critical" Deflection or point where curve deviates from linear law. This point depends on block dimensions and compound. When H=1·5 D it is about 55%
Modulus 270 lbs/sq in
Compound "A" only
Data obtained on static test.
Points relate to blocks of various dimensions (but H>D in all cases).
Blocks in same state of cure.
Similar curves of different slope are obtained with different compounds.

FIG. 8.—Relation between load per unit actual area and percentage deflection for cylindrical blocks under compression.

Using the relations established above, the following deductions may be made:

$$L=\frac{VE}{H}\,\Delta\left(\frac{1}{1-\Delta}\right)^{1.18}=\frac{VE}{H}X, \text{ where } V=\frac{\pi D^2 H}{4}$$

$$P=VE\Delta^2\left(\frac{1}{1-\Delta}\right)^{1.18}=VEY$$

$$W=\frac{VE}{0.1476}\left[\frac{1-0.18\,\Delta}{(1-\Delta)^{0.18}}-1\right]=VEZ$$

$$\frac{W}{P}=\frac{(1-\Delta)\left[1-0.18\,\Delta-(1-\Delta)^{0.18}\right]}{0.1476\,\Delta^2}=f(\Delta)=\frac{Z}{Y}.$$

Where $P=L\Delta H$ = product of load and deflection.

$$W=\int_0^{\Delta} LH\,d\Delta = \text{work done in deflecting from 0 to } \Delta.$$

Curves of X, Y and Z are given (along with some other properties of the functions) in Figure 9.

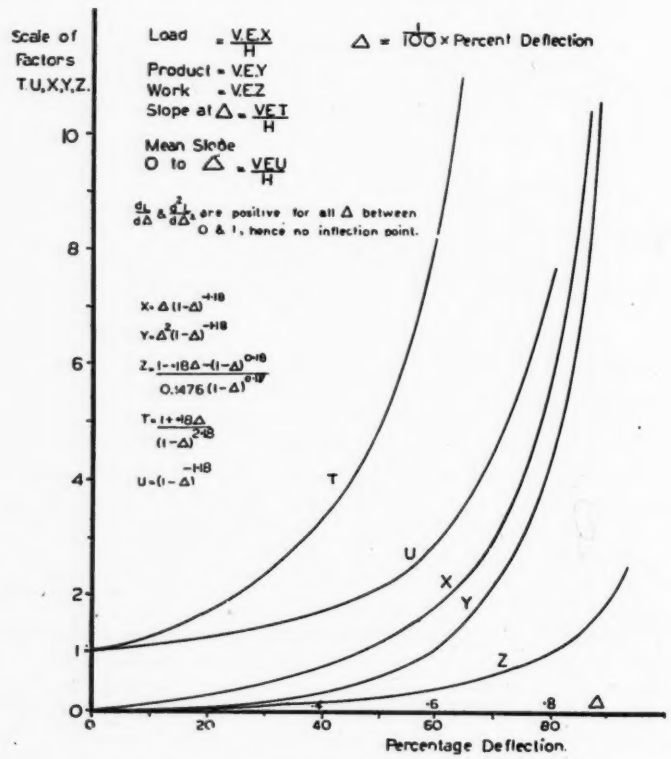


FIG. 9.—Factors for load, work, slopes, etc.

MODULUS.—The elastic modulus is defined as the slope of the line relating actual stress *i.e.*, the load divided by the deflected cross-sectional area, to actual deflection. This definition is perhaps slightly different from others which are found in the literature, but is presented for the following reasons. First, it is constant over the range where pure compression is obtained within the major part of the sample. Second, it is identical with the slope of the load per unit initial area-deflection line at zero deflection. Third, it is a parameter (which has the correct dimensional form), completely defining the load-deflection curve, provided the stress is purely compressive. The same value is obtained whatever the deflection used in making the necessary measurements to deduce it. And finally, it does not in reality differ from Young's Modulus, which is the rate of increase of stress with respect to strain. As engineers limit the term Young's Modulus to such small deflections that the question of deflected areas does not arise, it is evident that the present definition when applied to metals would give the standard result.

The relation between dynamic and static values.—The above relations are the direct outcome of what are termed static tests, and it was necessary to compare dynamic and static curves.

A clear definition of terms is absolutely essential. A static curve is considered to be the curve drawn through points representing the load and deflection in equilibrium and at rest. It is obtained by increasing either the load or deflection slowly to a given value and observing the two values when the motion has ceased. Hence, strictly speaking, the static curve is a line through the maximum load-deflection points of a series of cycles of various amplitude conducted at a static speed (such as 20 in. per min.).

By comparison it is clear that the equivalent dynamic curve is obtained by drawing a curve through the maximum load and deflection points of a series of cycles of various amplitudes taken at a speed, say, 3 cycles per second.

Dynamic curves, as defined, have been accurately compared with static curves, using the same blocks (compounds ranging from unloaded to heavily loaded). The dynamic curves were obtained by measuring the maximum load developed at various deflections, and the static and dynamic curves are in all cases identical within the limits of experimental error, that is, all points lie within 2 per cent, and the vast majority within 1 per cent of a common curve (see Figure 10 for some data), provided the following factors are carefully attended to: the load correction applied to the load measuring device with the latter operating with the correct piston movement; (2) the friction in the static load measuring device eliminated or allowed for; (3) any differences in load calibration of static test-machine and pressure-gauge readings on the load measuring cylinder allowed for, and (4) the same temperature of the block both curves are being obtained.

In these tests (1) amounted to 1 lb. per sq. in. (see Appendix A). The values of (2) 1.8 per cent, and (3) 0.4 per cent were obtained by dismantling the retaining flange and washer of the cylinder, and directly comparing the load-measuring cylinder with the static apparatus. (4) was ensured by working at room temperature, running only a few seconds for each dynamic point, and allowing ample cooling time.

The law relating to deflected diameter and height for static tests has also been shown to hold for dynamic tests by direct experiment (see crosses on Figure 7).

Further confirmation has also been obtained by means of an optical load-deflection recorder, which shows that the maximum load developed under a given

deflection when running at speed is within 1 per cent of that obtained if the machine is stopped and the belt pulled over slowly and brought to rest at maximum deflection. It must be clearly understood that it is not claimed that the transient curve of load and deflection traced in arriving at the maximum deformation is the same dynamically as statically, but merely that the curve through points instantaneously at rest is unaffected by the speed of compression, at least over the ranges of speeds mentioned. This means that the elastic constants are

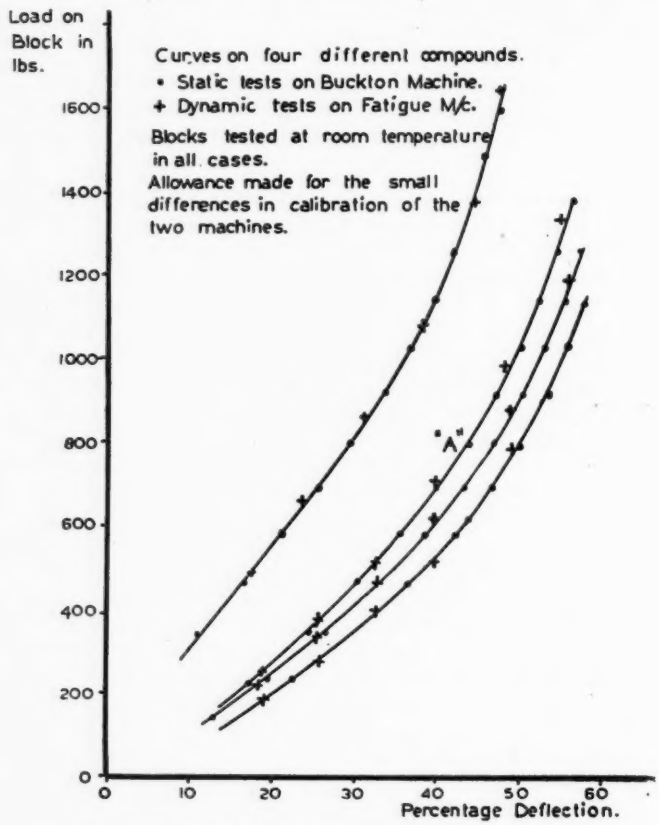
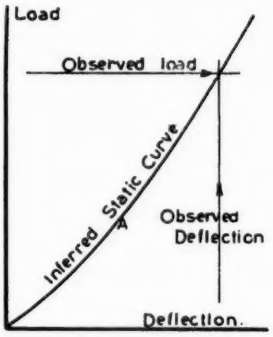


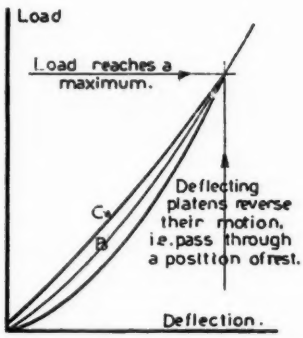
FIG. 10.—Observed static and dynamic load-deflection curves.

unaltered, *i.e.*, the modulus is the same. The actual transients will probably differ from this elastic curve, *i.e.*, the curve passing through the points at rest or cusps at the tops of the hysteresis loops, by an amount which depends on the instantaneous speed and the damping coefficient. Hence, although the modulus is the same dynamically as statically, the energy required to arrive at a given maximum load-deflection point probably differs in the two cases. These points are illustrated for a hypothetical case in Figure 11. It is important to realize that this is true of the static as well as the dynamic curve, and it is very likely that the actual transient in arriving at any point on the static curve is different from the static curve and not along it, as is usually implicitly supposed.

The dynamic transient for increasing load is sometimes taken as the dynamic curve, and is compared with the static curve previously defined; the comparison is then made between two physically different phenomena, *viz.*, the relation of load and deflection while movement is occurring and the relation where all points correspond to positions of rest. The curves relating to points obtained while



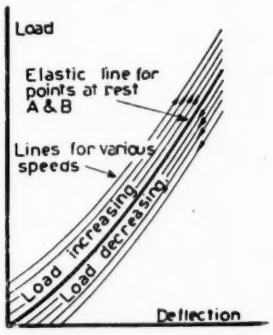
(*a*) Static load-deflection curve. Readings taken at rest.



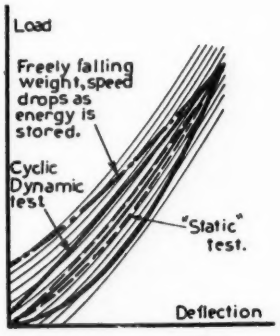
(*b*) Dynamic load-deflection elastic curve.
The elastic curve B passes through the cusps of transient hysteresis loops which are instantaneously at rest.

Curves A (static) and B (dynamic) are of similar definition, whereas curves A and C are not. Curves A and B are found to coincide on test (within experimental error).

Suggested form of transient load-deflection relationships.



(*c*) Probable load-deflection rate of loading relationships. The spacing of the curves is a function of the inherent damping properties.



(*d*) Transients arriving at a given maximum deflection depend on speed because of damping, not elastic differences. Maximum load unaltered, but greater energy required at high speed.

N.B.—Hysteresis energy appears as thermal energy (heat), and is not tored elastically.

FIG. 11.—Probable nature of static and dynamic relationships.

motion is occurring depend on the damping constant and speed of motion as well as on the elastic constants. Curves through points instantaneously at rest depend solely on the elastic constants, and are directly comparable.

Some investigators have indicated a difference between static and dynamic elastic constants even at the speeds now discussed. If those covered by the preceding discussion be excluded, it will be found that in general their work

belongs to one or other or both of the following two categories. First, two different physical methods are employed to obtain static and dynamic values, and these are not directly compared for calibration or other differences; secondly, the slopes of the load-deflection curve at two different deflections are compared, one being called the dynamic (usually a small range of deflection not near zero deflection) and the other called the static (usually the part of the curve extending to zero deflection). This is not sound, as the differences observed are present in both the static and dynamic curves, and are not a function of the speed of the test alone. The terms dynamic and static should refer to the effects consequent upon different rates of loading only.

The important fact established here is that the more accurately a dynamic-static comparison of rubber cylinders under pure compression is made at identical temperatures, the more nearly do the differences in elastic constants tend to disappear; they have been shown to be less than 1 per cent. It must be under stood that no conclusions regarding hysteresis loops are stated here, as these require further development of precise transient recorders.

Application of the Relations Established.—It is possible to proceed direct from the values of deflection, free height and load to modulus and work input by means of a set of curves (see Figure 12). The derivation of the graphs is as follows:

$$p=\frac{L}{A}=\frac{VE\Delta}{AH}\left(\frac{1}{1-\Delta}\right)^{1.18}=\frac{\pi D^2E}{4A}\Delta(1-\Delta)^{-.118}=KE\,f_0(\Delta).$$

Where p = air pressure, after inertia correction.

A = piston area.

$$W=VEZ \qquad P=VEY=L\Delta H$$

$$\therefore\left(\frac{W}{VH}\right)=\frac{EZ}{H}. \qquad \therefore\frac{P}{H}=\frac{VEY}{H}=\left(\frac{W}{VH}\right)V\frac{Y}{Z}.$$

$$\therefore p=\frac{L}{A}=\frac{P}{A\Delta H}=\frac{1}{A}\left(\frac{W}{VH}\right).\frac{V}{\Delta}.\frac{Y}{Z}.$$

$$=\phi\left[A,V,\left(\frac{W}{VH}\right),\Delta\right]$$

$$=\psi\left[\left(\frac{W}{V.H}\right),\Delta\right]$$ for a given value of A & V, as Y/Z is a function of Δ only.

Hence, provided the value of V remains constant, p is a function only of $\frac{W}{VH}$ and Δ.

With this form it is possible to construct one chart to cover blocks of various heights, whereas the original equations (p. 000) would have necessitated one chart per height. V is the volume of the undeformed block. The question of change of V with compression does not enter into this analysis, which is merely to discover a method of obtaining a chart suitable for blocks of varying heights.

Changes of V with fatiguing are so small that they can be ignored; they cannot be observed from volume estimations by displacement methods. More precise experimental confirmation has been obtained by comparing specific gravities of samples taken from the fatigued central parts of blocks and samples from

unflexed flange parts. Statistical analysis of the results shows that fatiguing up to the point of failure has no discernible effect on the density, even when the latter is measured with a standard error of one-sixth of one per cent.

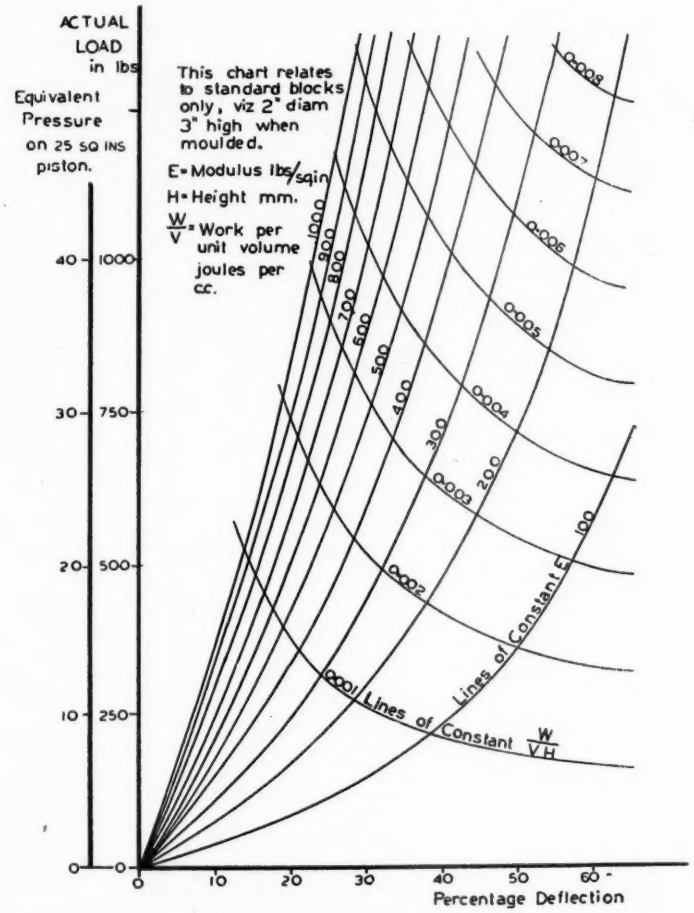


FIG. 12.—Chart of modulus and work relationships for fatigue tests. For machine operation, portions are drawn at a large scale, *viz.*, 25 mm. per cent deflection and per lb. gauge.

The x, y coördinates of the curves are taken as Δ and p, and curves joining points of equal values of E and $\frac{W}{VH}$ are drawn. Hence for a given set of values of p, Δ, H the required values of E and $\frac{W}{V}$ can be found (see Figure 12). For practical use, portions of these curves are drawn on a large scale.

General Behavior of Blocks under Test

These notes relate more directly to cylinders 2 inches in diameter by 3 inches high, tested at 0.5 Joules per cc., 3 cycles per second, carcass type compounds; changes from these conditions will have a corresponding effect on the behavior.

Temperature at the Centre of a Block.—During the first hour the temperature in the middle of the block rises rapidly to the region of 100 to 125° C, until the rate of heat loss is equal to the rate of heat generation. The rate of this rise is a function of the state of cure and is, in general, slowest at the optimum cure, judged by the Dunlop (Healey) Pendulum. The subsequent temperature curve depends largely on the original state of cure of the rubber. In the three general cases of (1) undercure, (2) optimum cure, and (3) overcure. (1) The temperature falls asymptotically to a steady value somewhat lower than

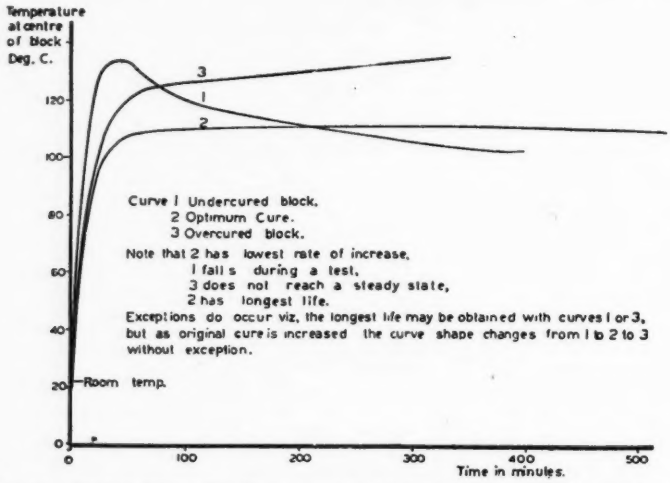


Fig. 13.—Typical temperature-time curves for blocks tested at constant work input.

the original maximum temperature. The greater the degree of undercure and the more prononunced is the early high temperature peak. (2) The temperature remains more or less steady at the maximum attained during the initial rise. (3) After the initial rapid rise, the temperature gradually increases throughout the whole of the time, with no true maximum temperature peak.

Of the three cases, that of optimum cure has in general the lowest mean temperature and the slowest initial rate of temperature increase. Undercured samples rise more rapidly in temperature than those which are overcured, but drop to lower final values. (See Figure 13.) After the initial peak the temperature appears to be a linear function of the logarithm of the time from start of test in all the above groups. The running temperature quoted in the results is the average of the mean temperatures of all the half-hour periods, neglecting the first four quarter hours.

Changes of Dimensions or Set.—In general the block height decreases throughout a test. In the early stages a slight increase of height (approximately 0.4 per cent) is sometimes observed, because of the temperature increase and because the consequent expansion is greater than the set. During the period when the temperature is rising rapidly, the rate of set slowly increases until,

at the point of maximum temperature, the set takes up a steady rate of increase with respect to the logarithm of the time from the start of the test.

The rate of set is defined as the percentage change of height during the period in which the time increases by ten times or its logarithm to the base 10 increases by unity.

The actual values of slope of the set-log time curves are reasonably constant, irrespective of the initial state of cure over the small range of cures tested, but the curves are displaced in the case of undercures towards early sets. Optimum and overcure curves lie closer together. The initial curved region is probably due to the effect of temperature on the rate of set; this would partly account for the rapid rise in set of undercured blocks. (See curves in Figure 14.)

A small loss of height occurs as a result of abrasion of the top surface of the block by the tool; this can be neglected, for in an extreme case it was found to

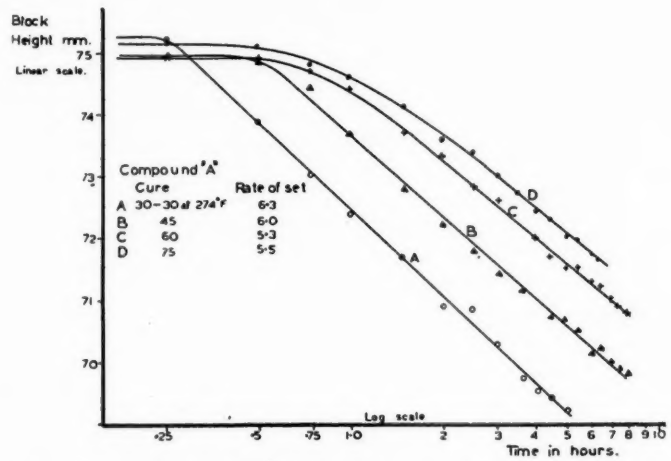


FIG. 14.—Rate of set curves showing linear relationship between set and logarithm of life.

be less than 0.2 per cent of the volume (and hence the height) of the block during the whole period of a test.

The total set on the block, from start of test to failure, decreases as the initial cure is increased. During the test the block changes from a cylindrical to a barrel shape; the set on the diameter following curves similar to those of the height.

CHANGES OF ELASTIC CONSTANTS.—The percentage deflection decreases rather rapidly during the warming-up period and thereafter at a slower rate. The load increases progressively during the test in the case of cures near the optimum.

Modulus follows similar laws with respect to time as the set on height, *i.e.*, after the warming period, the modulus varies linearly with the logarithm of the time. The slope of the curve depends on the initial state of cure and on the compound. Badly overcured blocks soften during the later stages of a test. Usually the compounds which give a good fatigue performance harden during a test when cured to their optima. Some gas black-loaded compounds soften during test. See Figures 15 and 15*a*.

POINT OF FAILURE.—The actual failure is detected by a drop in modulus associated, in some instances, with a sudden rise of temperature of a few degrees.

The internal split can often be confirmed by the feeling as the needle is inserted into the rubber when the temperature is being taken. As failure usually occurs between two readings, an estimate of the actual time to failure has to be made

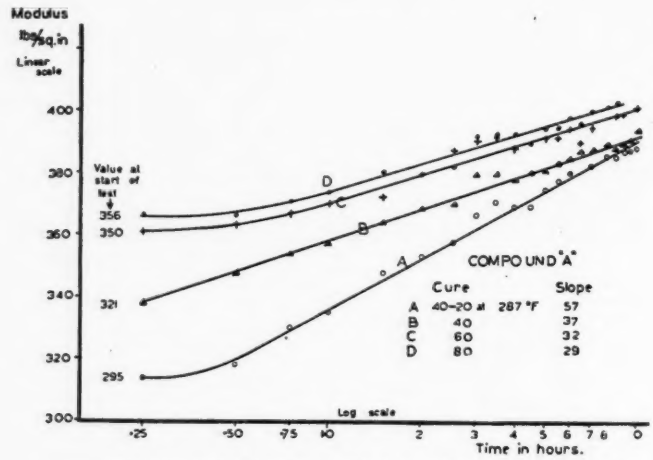


FIG. 15.—Modulus plotted against logarithm of life.

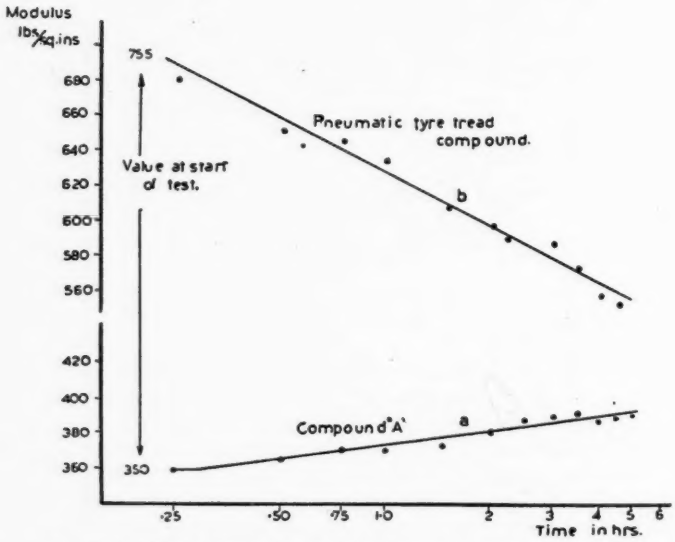


FIG. 15A.—Curves illustrating modulus changes of compounds which (1) harden, (2) soften, during a test.

from the extent of the breakdown when the block is cut up. The type of failure depends on the type of compound and severity of the test.

In carcass compounds the failed portion of the block at temperatures up to about 140° C bears some resemblance to an ordinary torn surface, with overcures giving a cleaner, straighter tear than undercures (see Figure 16). Under-

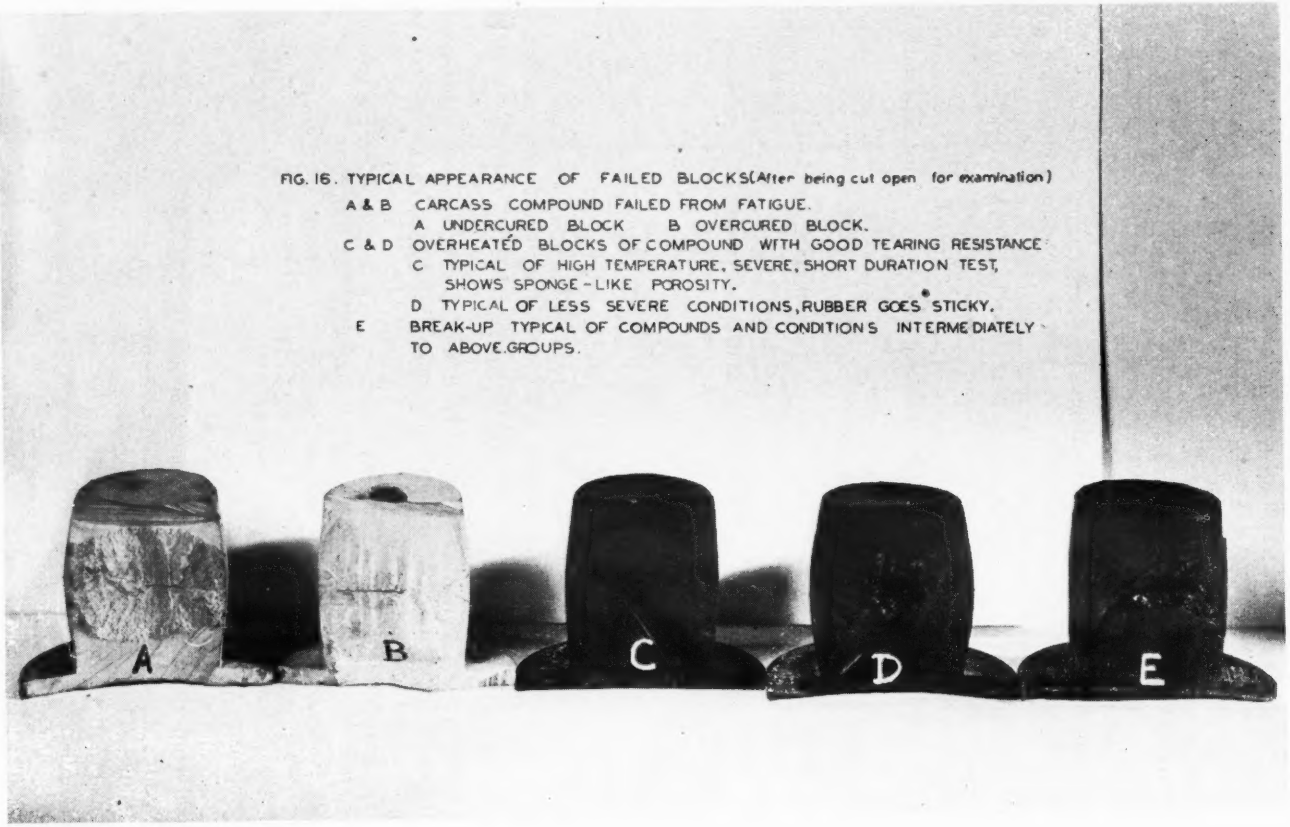


FIG. 16. TYPICAL APPEARANCE OF FAILED BLOCKS (After being cut open for examination)

A & B CARCASS COMPOUND FAILED FROM FATIGUE.
A UNDERCURED BLOCK B OVERCURED BLOCK.

C & D OVERHEATED BLOCKS OF COMPOUND WITH GOOD TEARING RESISTANCE
C TYPICAL OF HIGH TEMPERATURE, SEVERE, SHORT DURATION TEST, SHOWS SPONGE-LIKE POROSITY.
D TYPICAL OF LESS SEVERE CONDITIONS, RUBBER GOES STICKY.

E BREAK-UP TYPICAL OF COMPOUNDS AND CONDITIONS INTERMEDIATELY TO ABOVE GROUPS.

cured blocks do not develop their failures, after the initial stage of a small split inside, so rapidly as those which are overcured. The latter often split completely within a few minutes of the first sign of failure.

At the other extreme, mixings with high tearing resistance but high heat-generating characteristics, become porous if tested under conditions sufficiently severe to attain temperatures above 200° C in one hour or less. Under lower inputs these same mixings fail at lower temperatures, but the rubber becomes a sticky mass.

Compounds in which a good compromise between heating and tearing properties has been effected fail in a manner and at a temperature intermediate with respect to the sticky blow-out and the tearing types, that is, the failed portion of the block is dry but the rubber has broken short rather than torn, while the exposed surfaces discolor or take a slight gloss.

Relationship between Temperature and Life.—The following experimental relation (see Figure 17) appears to hold; for a rubber compounded to a constant formula.

Log $L_m = A - BT$ where L_m = life in minutes

This can be written T = mean running temp. (° C)

$L_m = C \times 10^{\frac{100-T}{D}}$ A and B are constants and C and D are related to A and B.

In a given case (compound A):

$C = 1740$ $D = 40$

and so $L_m = 1740 \times 10^{\frac{100-T}{40}} = 1740 \times 1.8^{\frac{100-T}{10}}$

And an increase of 40 centigrade degrees reduces the life to one-tenth of its former value, or 10 centigrade degrees reduces the life to just over one-half its value. This law is empirical and has not been widely tested outside the range of 100 to 130° C.

The corresponding life at 100° C can be estimated from this law. This is the probable life if the block is artificially maintained at 100° C. The law can be applied in the following alternative ways:

(1) Using life and mean temperature; this is the least precise, and is affected by state of cure.

(2) Plotting individual temperature readings on a graph of ordinates proportional to the exponential part of the above law and a uniform time abscissa. The area under the curve is the corresponding life at 100° C. The values are approximately independent of the cure over normal ranges tested.

(3) Using a factor table (derived from the law) and applying it to the individual temperature readings and summing the values. This agrees with (2).

Fatigue Resistance.—This is defined as the logarithm of the number of blows to failure. This figure is thought to convey a truer comparison of the relative merits of samples under review than the actual lives for the following reasons:

(1) All properties which progressively change during the test vary linearly with the logarithm of the life (or number of blows).

(2) The logarithm of the life is linearly related to the running temperature for any given compound.

(3) The ratio of the lives of blocks appears, from experience, to be a more

reliable measure of respective performances than the differences between the lives.

(4) Frequency curves plotted on a logarithm of life (or number of blows) base are a much closer approximation to a normal distribution than those plotted on bases proportional to life.

(5) Tests on blocks of various sizes indicate that, under comparable conditions of input, temperature and speed, the number of blows to failure is approximately independent of block size, whereas the life is altered in the ratio of the

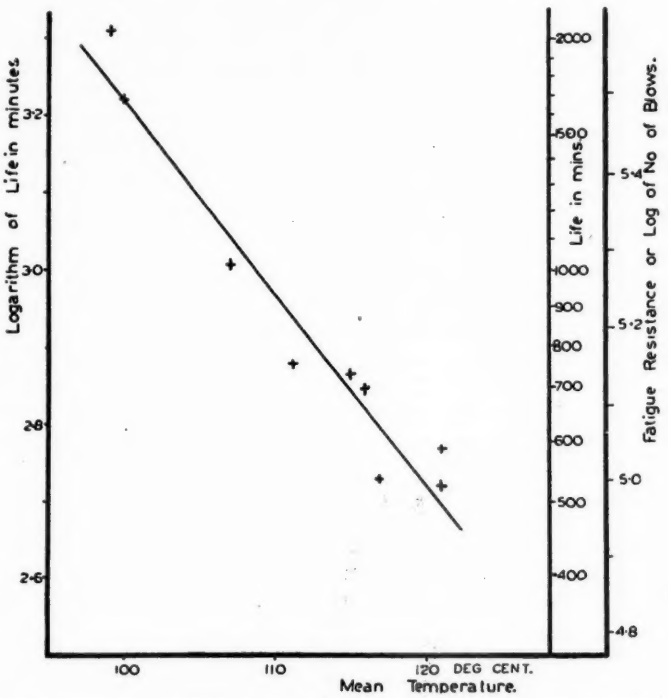


FIG. 17.—Relation between mean running temperature and logarithm of life for blocks of compound A.

speeds. It is for this reason that the logarithm of the number of blows is used in preference to the logarithm of the life.

It is further seen that the corresponding life at 100° C (L_{100}) can be related to the fatigue resistance R, obtained at a mean running temperature T, by the equation:

$$R = \log L_{100} + \log n + \frac{100 - T}{40},$$

where n is number of blows per minute.

On the same basis, and subject to the limitations already stated, the fatigue resistance R, obtained at temperature T, can be converted to its equivalent value R_0 at any temperature T_0 by the expression: $R_0 = R_1 + \frac{T_1 - T_0}{40}$.

MISCELLANEOUS POINTS

ROOM TEMPERATURE.—The machines were originally installed in building A, and as it was shown that variations of the ambient temperature were important, they were removed to a controlled temperature building B (Table I).

A statistical analysis of the data on tests carried out on blocks in building A shows that 1 centigrade degree change in room temperature results in 1.233 ± 0.039 C degrees change in block running temperature. For practical purposes 1: 1.25 is taken as the ratio, and the data show that the value is independent of the compound under test.

TABLE I

ROOM TEMPERATURE ° C.

	Temperatures (° C.) actual values			Daily average values		
	Max.	Min.	Range	Max.	Min.	Range
A	32.3	9.0	23.3	28.0	10.2	17.8
B	24.6	18.6	6.0	22.8	19.4	3.4

TABLE II

MEAN ERRORS

(Errors which are functions of the machine and method of operation only)

	Mean error of individual readings		Mean error of mean result for whole test	
	Value	Percentage	Value	Percentage
Temperature (Centigrade degrees)	1.5	—	1.5	—
Load (lbs. per sq. in.)	0.1	0.5	—	—
Height and deflection	0.05	—	—	—
Work input and modulus—				
(1) Variation from a constant value	—	0.3	—	0.5
(2) Error from absolute value	—	1.0	—	1.5
Speed (r.p.m.)	0.5	0.25	1.0	0.5
Failing point in terms of fatigue resistance value	—	—	0.02	0.5
Expected error in fatigue resistance, *i.e.*, all above combined plus effect of room temperature	—	—	0.06	1.5

EFFECT OF STOPS FOR OBSERVATIONS.—The machine is stopped for 1.5 minutes for observations at definite times during all tests (see above). The effect of these stops is to cool the testpiece slightly and hence to prolong its life. As the same procedure is always adopted, the effect of the stops is ignored.

Long stops in the middle of a test have an unknown effect on the result. This point has not been sufficiently investigated to apply a correction; in any case the probable effect is not a change in the relative order of results, as care is taken to ensure that blocks which last longer than one day complete at least 420 minutes' test before the first stop. This allows the block to attain steady running conditions for some hours before the first stop. In the great majority of cases the only long stops are those which occur overnight.

EFFECT OF NEEDLE HOLE.—Any variability in the results which might be due to the repeated penetration of the test piece by a thermojunction needle is minimized by the use of a blunt instrument, which always enters the same hole. The hole is originally made by a sharply pointed wire and its presence tends to

localize the position of the failure, without having a serious effect in reducing the period of running before failure.

ERRORS.—The possible sources of errors have been studied and the method of their determination indicated in Appendix B. Mean errors were used rather than standard (or root-mean-square) values, as the extra complication of these latter was not considered justifiable. The main findings are tabulated in Table II. Careful operation is, of course, essential to maintain this high standard.

Standard errors equal 1.25 times the mean errors, and the maximum error in any individual reading (only encountered once during any one test involving approximately 20 readings) is less than four times the mean error.

ACCURACY OF REPETITION. Tables III-A to III-D show the results of tests carried out on eight blocks, cured four at a time at 274° F, to check the accuracy of repetition.

To state from one test on each of two blocks that a given difference is significant (taking a 0.05 level of significance or one chance in twenty that the difference is a random deviation), it must exceed three times the above standard deviations. For cases where more than one block of each is tested the reader is referred to a work by Fisher[11]. An increased number of tests results in the detection of smaller differences.

Using Fischer's *"z test"*, it is found that both machine and curing condition differences fail to reach the 0.05 level of significance when compared with experimental and rubber variations. The nearest approach to this level is in the case of the running temperatures of specimens cured at a different time. "Students test" (see Fisher[11]) confirms that the two machines give results not statistically different, although it suggests that the chances that blocks cured separately are members of an identical population are less than one in a hundred.

The above findings indicate that some difference exists between two blocks cured at different times, but that blocks in the same cure are substantially the same. No detectable difference exists between the two machines.

The mean deviations broadly confirm the values given in Table II. The slightly larger variation of fatigue resistance is in all probability due to the variability inherent in the rubber compounds, a fact which is a major difficulty of fatigue testing.

METHOD OF TABULATING RESULTS.—The more important figures which are quoted as the result of a fatigue test are: (1) fatigue resistance, (2) mean running temperature, (3) modulus at start and finish of a test, (4) rate of set on height, and (5) change of modulus during a test.

The average values of (1) work input per cc. of rubber per cycle, (2) machine speed, and (3) room temperature are noted in connection with each test.

APPLICATION OF FATIGUE TEST TO COMPOUNDING PROBLEMS

EFFECT OF VARYING TESTING CONDITIONS ON DIFFERENT TYPES OF COMPOUND.—Results are shown in Table IV on five compounds as under:

	B	C	D	E	F
Rubber	100	100	100	100	100
Sulfur	3	3	3	3	3
Mercaptobenzothiazole	1	1	1	1	1
Stearic acid	3	3	3	3	3
Antioxidant	1	1	1	1	1
Zinc oxide	5	55	160	5	5
Lamp black	—	—	—	50	—
Gas black	—	—	—	—	50
Modulus (lbs. per sq. in.)	275	370	515	685	665

Compound B is a pure gum type, C is a tire-carcass type; D, E and F have equivalent volume loadings of filler; F is a pneumatic-tread type.

Among the points worth noting on Table IV are that compound E is consistently good, compound F runs consistently hot, and the relative order by the

TABLE III-A

REPETITION TESTS ON COMPOUND A

First Cure

Machine No.	Fatigue resistance	Running temp. (° C.)	Room temp. (° C.)	Work input (J/cc.)	Rate of set	Modulus Start	Modulus Finish	Rate of change
2	4.70	134	20.1	0.500	8.0	262	328	66
1	4.46	134	20.0	0.495	8.3	262	317	55
2	4.60	135	20.1	0.501	8.1	266	326	60
1	4.54	135	20.0	0.500	7.9	263	318	55

Second Cure

1	4.80	130	20.5	0.501	7.7	270	334	64
2	4.70	131	20.4	0.504	6.8	270	337	67
1	4.98	130	20.2	0.502	7.2	270	340	70
2	5.00	131	20.2	0.503	6.7	270	340	70

TABLE III-B

AVERAGE VALUES

	Fatigue resistance	Running temp. (° C.)	Room temp. (° C.)	Work input (J/cc.)	Rate of set	Modulus Start	Modulus Finish	Rate of change
First cure	4.58	134.5	20.1	0.499	8.1	263	322	59
Second cure	4.87	130.5	20.3	0.503	7.1	270	338	68
Both cures	4.72	132.5	20.2	0.501	7.7	267	330	63
Machine 1	4.69	132	20.2	0.500	7.8	266	327	61
Machine 2	4.75	133	20.2	0.502	7.4	267	333	66

TABLE III-C

MEAN DEVIATION

(Percentage on average values (except in case of temperatures)

	Fatigue resistance	Running temp. (° C.)	Room temp. (° C.)	Work input (J/cc.)	Rate of set	Modulus Start	Modulus Finish
First cure	1.6	0.5	0.5	0.4	0.8	0.5	1.5
Second cure	2.5	0.5	0.1	0.2	3.9	0.0	0.7
Both cures	3.2	2.0	0.1	0.35	6.4	1.3	2.4

TABLE III-D

STANDARD DEVIATIONS

Comparison	Fatigue resistance	Running temp. (° C.)	Rate of set	Modulus start (lbs. per sq. in.)
All tests both machines and cures.....	0.18	2.1	0.54	5.3
Tests on same machine from same cure...	0.145	0.5	0.15	1.5

four methods of testing indicates clearly the necessity of choosing conditions similar to those applying in service. Thus, to take an extreme case, if vulcanizates intended for use as solid tire treads are compared under conditions of constant percentage deflection or constant deflected height, low modulus compounds like

B and C behave better than E, a more usual solid tire type. Under constant load conditions the compounds are placed in the right order.

Effect of Vulcanizing Time and Temperature on Fatigue Properties.—Compound A was chosen for this work. Tests were carried out under conditions whereby the product of load and deflection was kept at a constant figure approximating to an energy input of 0.45 to 0.5 joules per cc. At the time the tests were made, the method to produce accurate constant work conditions had not been developed.

Table IV

Effect of Varying Testing Conditions on Different Compounds

Compound	Life (min.)	Fatigue resistance or logarithm of no. of blows	Temperature (° C.)
Constant work (0.5 Joules per cc.)			
B	275	4.71	98
C	460	4.94	112
D	100	4.27	192
E	3620	5.83	121
F	50	3.97	240
Constant load (50 lbs. per sq. in.)			
B	375	4.85	98
C	545	5.01	106
D	120	4.35	119
E	4000 not failed	5.88+	108
F	70	4.12	224
Constant percentage deflection (40 per cent)			
B	4120 not failed	5.89+	56
C	4000 not failed	5.88+	70
D	270	4.70	162
E	995	5.27	141
F	30	3.70	218
Constant deflected height (42 mm.)			
B	390 *not failed	4.86+	69
C	525 *not failed	4.99+	87
D	170	4.50	197
E	530	5.06	160
F	30	3.70	270

* These samples would obviously have run several thousand minutes.

Figure 18 shows the relation between the time of vulcanization and various properties measured on the fatigue machine. The time of cure chosen for optimum is that which most nearly conforms to the following: (1) the cure for longest fatigue life, (2) the cure for lowest mean running temperature, (3) the cure for lowest peak temperature, (4) the cure where the peak temperature and the temperature after three hours' running are equal, *i.e.*, the block runs at a steady temperature, (5) the cure at which the time to the start of uniform logarithmic rate of set ceases to increase rapidly with cure.

There is a suggestion from the trend of the curves that fatigue resistance is

reduced at higher vulcanizing temperatures, but that within the range of 15 and 50 lbs. steam pressure the change in properties is negligible.

The relation between the time of equivalent optimum cure and the temperature of the cure is shown in Figure 19. The points lie on a straight line, and from

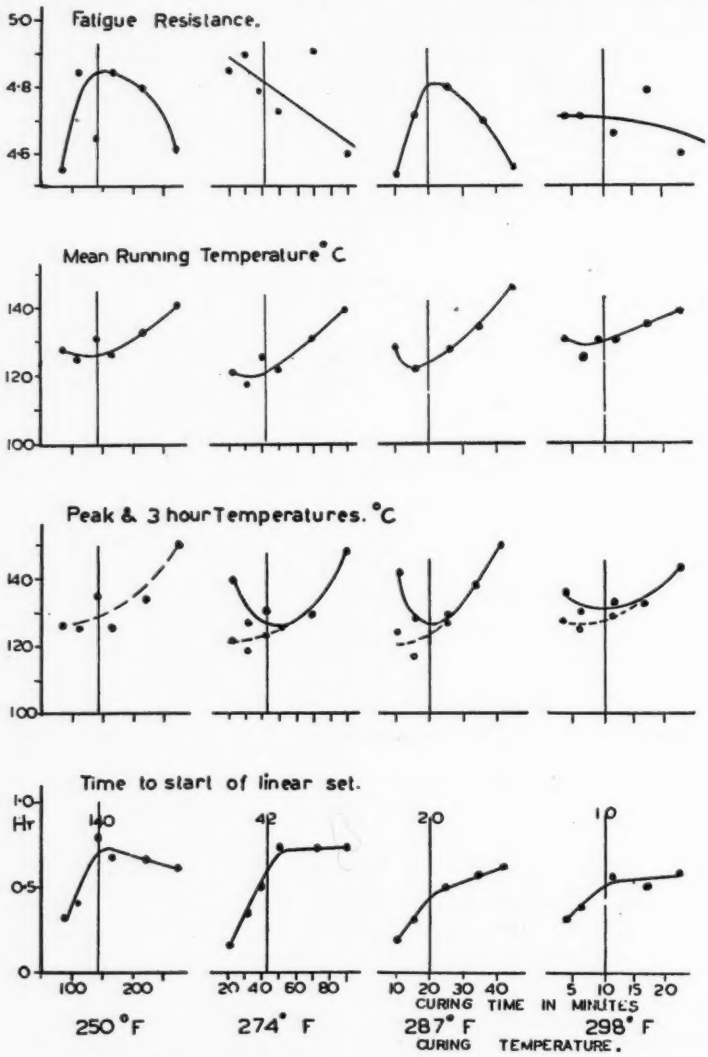


FIG. 18.—Properties of blocks cured at various temperatures.

its equation it can be shown that, as the curing temperature is reduced by 10 centigrade degrees, the curing time is increased in the ratio of 2.3 to 1. This value of 2.3 for the temperature coefficient of mercaptobenzothiazole-accelerated compounds compares with figures varying from 1.9 to 2.3 which have been obtained by other methods by Gerke[12].

EFFECT OF RAW RUBBER VARIATION ON FATIGUE PROPERTIES OF VULCANIZATES.—Table V gives the results with compound A at optimum cure (judged by fatigue testing) of eight samples of smoked sheet rubber chosen at random from different estates and on a blend of these eight samples. The testing conditions were the same as those indicated above. In Figures 20 and 21 the fatigue resistances and running temperatures are plotted over a range of cures for three of these samples, including the best and two of the worst, and of the blend of the whole eight. The results show considerable variability, not only in fatigue

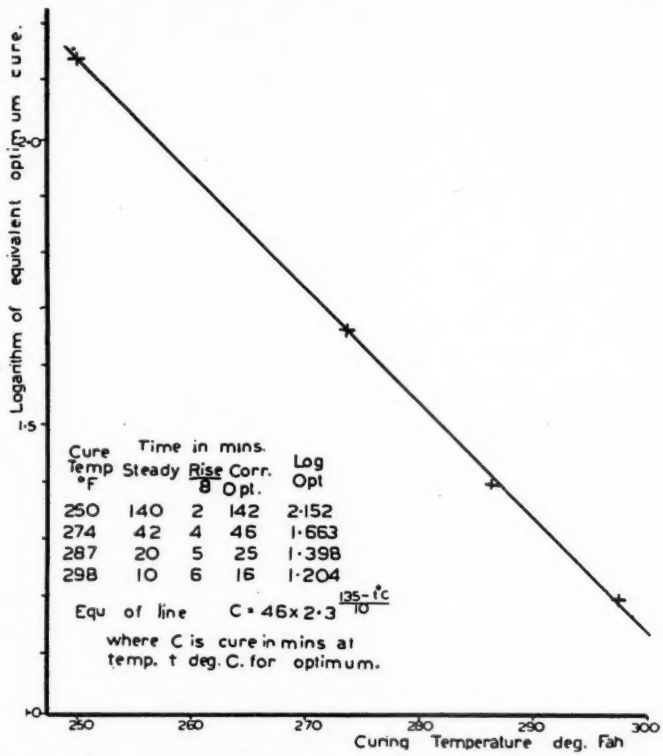


FIG. 19.—Relation between logarithm of time of cure for optimum properties and curing temperature.

properties, but also in rate of cure. There is a suggestion that blending produces flatter curing properties.

Table VI illustrates variability of rubber from the same source, test figures from samples from each of two estates being quoted.

This variation of rubber from the same and different estates has been further shown by overheating tests on solid tire tread stocks.

EFFECT OF PLASTICITY ON FATIGUE PROPERTIES.—Compound A was chosen for this investigation, and the testing conditions were the same as in the work just discussed. Stocks from the same sample of raw rubber were masticated to different plasticities and mixed on a laboratory mill. Results of fatigue and pendulum tests at optimum cure are figured in Table VII.

These results show that fatigue resistance is at a maximum with a moderate degree of mastication, but that excessive milling causes a drop in fatigue life with a greater heat development and higher rate of set. A fall in initial modulus accompanies the increased plasticity.

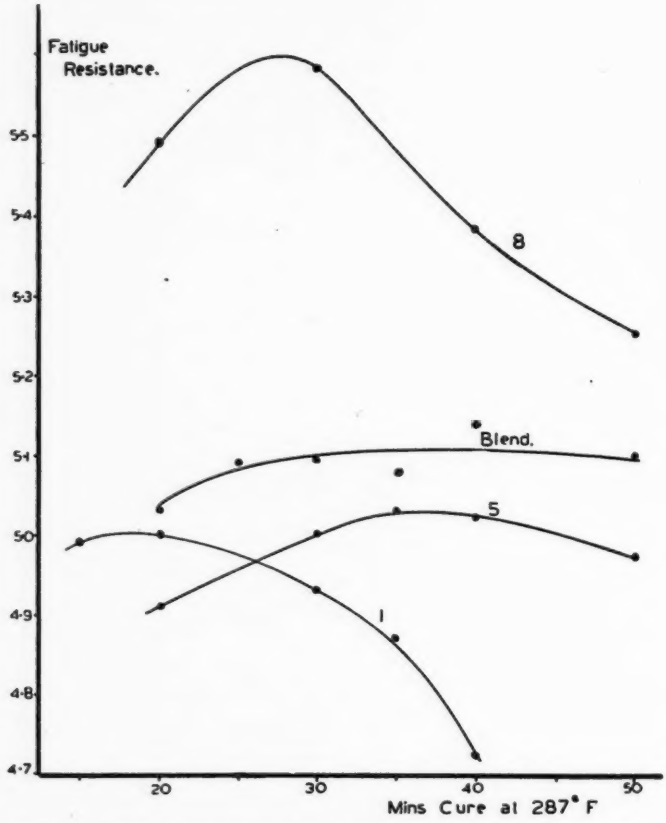


FIG. 20.—Effect of raw rubber on the fatigue resistance-curve of compound A. Selected curves from eight estates. Numbers on curves refer to Table V.

TABLE V

EFFECT OF RUBBER FROM VARIOUS SOURCES. RESULTS OF TESTS AT OPTIMUM CURE

Smoked sheet	Optimum cure (min. at 287° F.)	Life in min.	Fatigue resistance	Mean running temp. (° C.)	Rate of set	Modulus at start of test
No. 1 estate	20	540	5.00	117	5.0	270
" 2 "	20	1660	5.50	100	4.4	295
" 3 "	35	1020	5.29	107	4.2	300
" 4 "	35	565	5.01	121	5.3	295
" 5 "	35	580	5.02	120	5.5	320
" 6 "	35	760	5.15	112	4.7	315
" 7 "	30	700	5.12	116	5.2	305
" 8 "	30	2040	5.58	99	4.0	320
Blend of above	40	730	5.14	108	4.8	310

The effect of pine tar was next investigated, the same basic compound being used. The same milling treatment was accorded to a series of stocks containing increasing quantities of softener made from a sample of smoked sheet (not the same as that used above), masticated to a plasticity of 2.8. In the table, the pine tar content is expressed as percentage of the whole compound and not of the rubber alone (see also Figure 22).

The results (Table VIII) show that excess of pine tar causes a serious drop

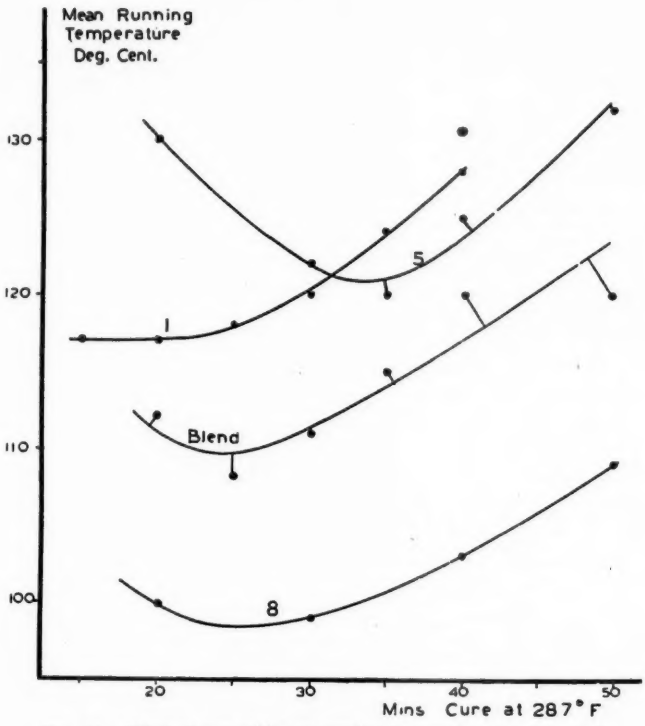


FIG. 21.—Effect of raw rubber on running temperature-cure curves of compound A. Curves for same estates as Figure 20.

TABLE VI

VARIABILITY OF RUBBERS FROM TWO SOURCES. RESULTS OF TESTS OF OPTIMUM CURES

Smoked sheet	Optimum cure (min. at 287° F.)	Life in min.	Fatigue resistance	Mean running temp. (° C.)	Rate of set	Modulus at start of test
No. 8 Estate.						
(*a*)	30	2040	5.58	99	4.0	320
(*b*)	20	1270	5.38	101	5.2	295
(*c*)	30	940	5.25	103	3.7	320
(*d*)	25	320	4.78	132	6.4	270
No. 9 Estate.						
(*a*)	40	390	4.87	135	7.1	340
(*b*)	30	480	4.96	119	6.3	310
(*c*)	20	525	4.99	120	5.0	305
(*d*)	20	370	4.84	129	7.2	305

in fatigue resistance of the vulcanizate without further softening of the uncured compound. It is interesting to note that, although pine tar in moderate proportions considerably increases heat generation during fatiguing, the resilience at 50° C is unaffected.

TABLE VII

EFFECT OF PLASTICITY ON PROPERTIES AT OPTIMUM CURE

Mastication time (minutes)	Extrusion plasticity of raw rubber *	Compression plasticity of mixed rubber †	Optimum cure (min. at 30 lb. per sq. in.)	Life (min.)	Fatigue resistance	Mean running temp. (° C.)	Rate set	Modulus (lb. per sq. in.) at start	Pendulum resilience (per cent)
9	4.0	385	60	500	4.98	112	4.0	310	88.7
20	2.3	445	60	640	5.07	110	3.8	310	88.4
50	0.7	565	60	365	4.85	127	5.7	300	87.0
150	0.2	665	60	250	4.68	136	6.2	295	86.7

* Time in minutes to extrude a cylinder of rubber 2 cm. in depth and 2.54 cm. diameter through an orifice 0.24 cm. diameter with 700 lb. load on the 1 in. diameter cylinder. Temperature 85° C.
† Depression in 0.01 mm. of cylinder of rubber, between two plates. Load 600 g. Temperature 85° C. Cylinder dimensions: 1 cm. diameter; 1 cm. height.

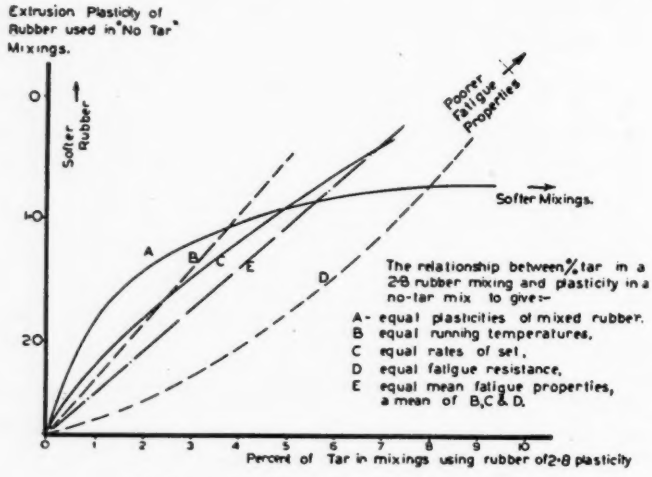

Extrusion Plasticity of Rubber used in "No Tar" Mixings.
0
5
20
Softer Rubber
Poorer Fatigue Properties
Softer Mixings.
A
B
C
E
D
The relationship between % tar in a 2·8 rubber mixing and plasticity in a no-tar mix to give:-
A- equal plasticities of mixed rubber.
B equal running temperatures,
C equal rates of set,
D equal fatigue resistance,
E equal mean fatigue properties, a mean of B,C & D.
0 1 2 3 4 5 6 7 8 9 10
Percent of Tar in mixings using rubber of 2·8 plasticity

FIG. 22.—Comparison of pine tar and mastication.

TABLE VIII

EFFECT OF PINE TAR ON PROPERTIES AT OPTIMUM CURE

Pine tar (per cent)	Compression plasticity of mixed rubber	Optimum cure (min. at 30 lb. per sq. in.)	Fatigue life (min.)	Fatigue resistance	Mean running temp. (° C.)	Rate of set	Modulus		Pendulum resilience (per cent)
							Start	Finish	
0	405	60	300	4.74	124	4.7	290	355	86.7
1	400	60	440	4.93	124	5.7	285	355	86.4
2	470	60	270	4.71	128	6.5	280	345	86.7
3	480	60	320	4.77	130	5.3	275	330	86.7
5	545	60	285	4.74	145	7.1	260	350	86.4
10	540	60	80	4.17	—	10.5	255	305	87.0

Figure 22 is an attempt to show graphically the relation between the percentage of pine tar in rubber of plasticity 2.8 and the plasticity required when no tar is used to obtain (1) equal mixed-rubber compression; (2) equal running temperature during fatigue testing; (3) equal rates of set; (4) equal fatigue lives, and (5) equal mean fatigue resistance (the curve for (5) is the approximate mean of those for (2), (3) and (4)). It shows that pine tar up to 3 per cent can be used with advantage over the range where the plasticity curve lies above the fatigue curves. At high tar contents, a large increase in softener is necessary to effect the same change in unvulcanized rubber compression that would be caused by a small change in plasticity as a result of increased mastication and, as shown, would cause a considerable diminution of fatigue resistance. More work is needed to show how far this principle can be extended to different types of compound.

The effect of varying plasticity in unmasticated rubber has also been investigated, and Table IX gives the results of tests on two lots of rubber of greatly different plasticity which were masticated for various times to enable comparisons to be made between rubbers of equal mastication time, equal plasticity of masticated rubber, and equal mixed rubber plasticity. At all plasticities the initially hard rubber produced vulcanizates distinctly superior to those mixed from the soft rubber.

Extensive testing has shown that for the most part initially hard (low-plasticity) rubbers give vulcanizates with better fatigue properties than soft rubbers. This statement applies to compounds accelerated by mercaptobenzothiazole alone, and even in the case of such compounds, it should not be accepted as a universal principle on account of the exceptions which have been found to it.

Effect of Sulfur-Accelerator Ratios on Fatigue Properties.—A carcass-type stock containing lamp black was chosen for this investigation. Two series of compounds were tested (1) accelerator constant ($\frac{3}{8}$ per cent on rubber) sulfur $2\frac{1}{3}$, 3, $3\frac{3}{8}$, $4\frac{1}{3}$ and 5 per cent on rubber, and (2) sulfur constant ($3\frac{3}{8}$ per cent on rubber), accelerator (mercaptobenzothiazole) $\frac{1}{3}$, $\frac{1}{2}$, $\frac{3}{8}$, $\frac{5}{8}$ and 1 per cent on rubber. The tests were made under constant energy input conditions of 0.5 joules per cc.

Figures 23 and 24 show that fatigue resistance improves as both sulfur and accelerator are increased. Pendulum resilience similarly increases. In practice the upper limit of sulfur and accelerator are fixed by cure and scorching considerations, and by the relative importance of fatigue and other properties.

This point is illustrated in Figure 25, which compares tearing resistance, fatigue resistance and resilience at the 50 minutes' cure of the sulfur series of compounds now under consideration. The tear resistance is expressed as the force in pounds to tear a block of rubber one inch thick. (The details of this test have not been published). The curves show that high sulfur, although improving fatigue, has an adverse influence on resistance to tear.

Effect of Cheap Fillers and Reclaim on Fatigue Properties.—Four compounds of almost identical cured hardness but containing different fillers: (1) lamp black, (2) whiting, (3) china clay and alkali whole-tire reclaim, (4) whiting and alkakli whole-tire reclaim, were compared for fatigue resistance under conditions of 0.4 joules per cc. energy input. Figure 26 shows that (3) and (4) have lower resiliences than (1) and (2), much lower fatigue resistance than (2), and very much lower fatigue resistance than (1). The comparison of (1) and (2) is interesting, for, although (2) has a slightly higher resilience than (1) at 50° C it develops more heat during fatigue. At 100° C, the order of the resili-

TABLE IX

COMPARISON OF HARD AND SOFT RUBBER WITH VARIOUS MASTICATION TIMES

Initial extrusion plasticity	Mastication (min.)	Extrusion plasticity of masticated rubber	Compression plasticity of mixed rubber	Optimum cure (min. at 30 lbs. per sq. in.)	Fatigue life (minutes)	Fatigue resistance	Mean running temp. (° C.)	Rate of set	Modulus		Pendulum resilience (per cent)
									Start	Finish	
73.5 (hard)	15	3.0	420	45	2090	5.60	96	4.8	315	395	88.1
73.5 "	20	1.8	450	45	2265	5.63	93	3.6	320	385	87.6
73.5 "	30	0.8	505	45	1815	5.53	100	5.2	300	390	86.4
73.5 "	50	0.5	595	45	1580	5.47	101	5.1	305	395	86.7
9.9 (soft)	10	3.3	445	60	475	4.95	132	5.6	280	355	85.4
9.9 "	12	2.9	455	60	420	4.90	138	5.5	270	350	85.1
9.9 "	15	1.4	460	60	390	4.87	131	5.6	260	335	85.7
9.9 "	20	1.0	480	60	560	5.02	127	5.6	290	360	85.4

ences of these two compounds is still unchanged, and their thermal conductivities are similar. It can, therefore, reasonably be concluded that the higher running temperature results from a change in properties due to the fatiguing action on the rubber.

Estimation of Power Loss.—By noting the temperature-time curves during and after a test, a curve of temperature rise, assuming no loss of heat due to cooling, can be drawn. The slope of this line (in appropriate units) is a measure

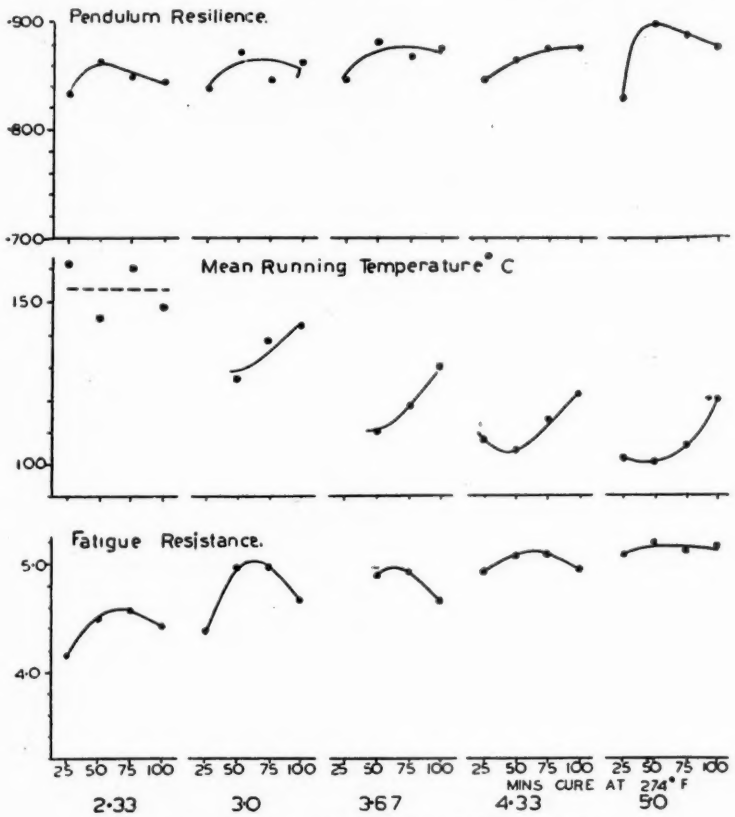


Fig. 23.—Effect of sulfur content on fatigue properties.

of the power loss or energy dissipated by hysteresis (Method *a*). Alternatively the ratio of the rate of heat energy loss to the rate of work input at a given steady temperature is a measure of power loss (Method *b*). Some results are given in Table X, and a comparison with existing methods is included.

The last column is the difference between the resilience value and 100 per cent; this was taken instead of the power loss at constant force[13], since the samples were compared at constant energy input, which is also the condition of resilience measurement on the pendulum.

The agreement between the pendulum and the present test is affected by the fact that all pendulum data relate to the value at 50° C, whereas method (*b*)

relates to the value in the sixth column, and method (*a*) gives a value which is mainly dependent on that temperature and to some extent on lower temperatures.

COMPARISON OF EFFECTS OF MECHANICAL WORK AND HEATING

The importance of the heating effect in promoting deterioration during fatigue testing has been emphasized in the foregoing pages. The following evidence

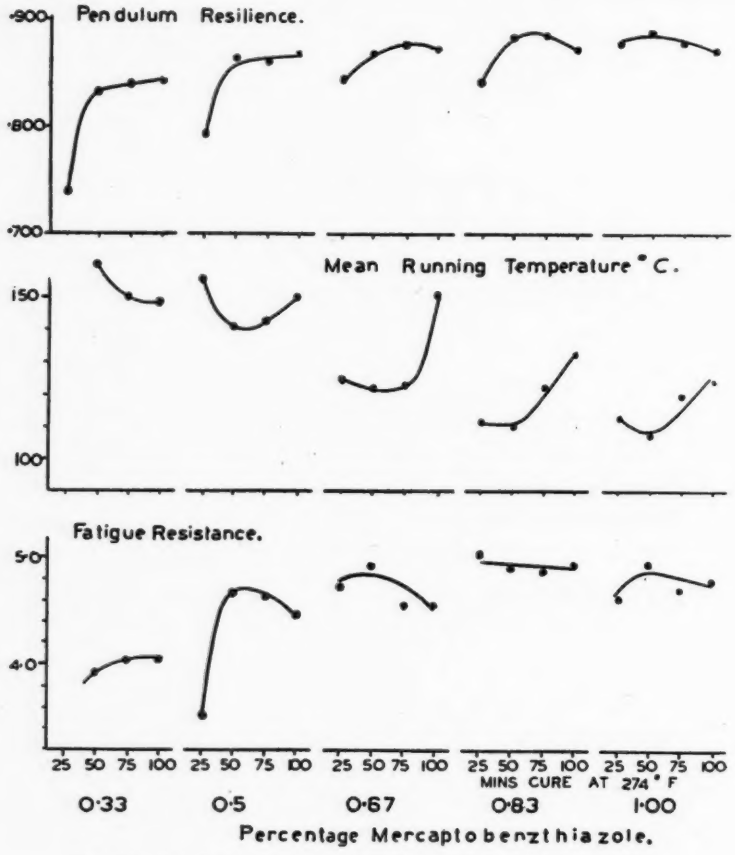


FIG. 24.—Effect of mercaptobenzthiazole content on fatigue properties.

is adduced to show that mechanical work also is an essential part of the test and that failure is not produced merely by heating the rubber.

Test pieces were heated in an oven at 100° C for times (1) equal to their corresponding lives at 100° C, and (2) seven times as long. The results show that the blocks after this drastic heat aging have remarkably good lives—in the case of (2) 10 per cent below normal, and (2) 40 per cent below normal. The respective falls in fatigue resistance, as defined in this paper, are 0.05 and 0.22.

TABLE X

ESTIMATION OF POWER LOSS FROM TEMPERATURE CURVES

Tests carried out at 0.25 joule per cc. (approx.) 3 times per second

Compound	Specific gravity	Calc. specific heat	Modulus start of test (lbs. per sq. in.)	Temperature (° C.)		Energy (joules per cc.)		Power loss (percentage)				
				Observed steady value	Value which would obtain at 3 hrs with no cooling	Loss, *i.e.*, equiv. to previous column	Total input	Fatigue machine Constant energy input			Pendulum	
								Method (*a*)	Method (*b*)	Mean of (*a*) and (*b*)	Constant force	Constant energy
Carcass	1.011	0.46	340	51	175	342	7950	3.8	4.3	4.0	14.0	4.0
"	0.960	0.49	280	58	200	394	7855	5.1	5.0	5.1	—	—
"	1.270	0.37	345	66	255	504	7780	6.5	6.5	6.5	19.5	9.0
"	1.265	0.37	355	75	325	625	7819	8.4	8.2	8.3	21.0	9.5
"	0.980	0.47	220	85	365	706	7940	8.9	8.0	8.5	28.0	10.5
Solid tire	1.244	0.36	790	79	395	727	7590	9.2	9.6	9.4	16.5	13.0
Carcass	0.970	0.48	205	97	465	910	8030	10.2	11.3	10.7	—	—
Cheap carcass	1.125	0.41	350	98	475	920	7880	11.3	11.7	11.5	21.0	9.5
Acetylene black tread	1.245	0.36	1220	94	540	994	8170	11.5	12.2	11.8	16.0	23.7
Pneumatic tread	1.110	0.40	500	157	1020	1901	7480	26.2	26.2	26.4	37.0	31.0

Further evidence has been obtained from tripsometer testing of specimens before and after fatiguing (the Dunlop Tripsometer is a form of pendulum designed to test small samples). Table XI shows hardness and resilience figures on two

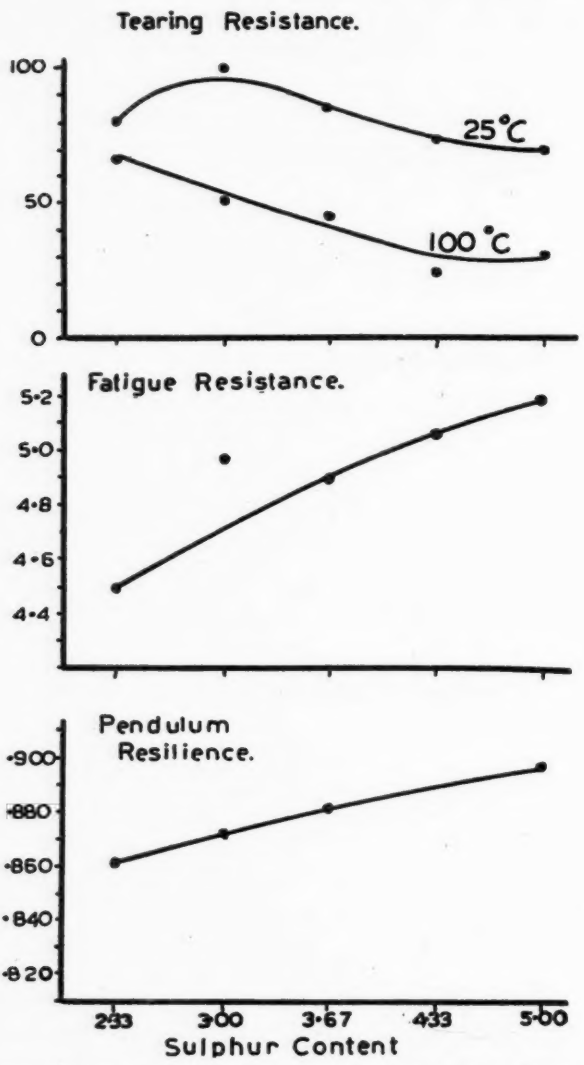


FIG. 25.—Effect of sulfur content on related properties. Values refer to 50-minute cure.

samples cut from each of two blocks of identical compound and cure, one of which had been fatigued for a prolonged period. The results show that the hysteresis properties are not significantly changed by the fatiguing action, and emphasize the importance of mechanical work in producing breakdown of rubber.

The case is different when failures of the thermal decomposition type are obtained. Figure 27 shows time-temperature relations of a solid tire compound stressed under a constant load of 25 cwt. The test-piece is a block of rubber 2.5 in. square and 4 in. high. The temperatures are autographically recorded once

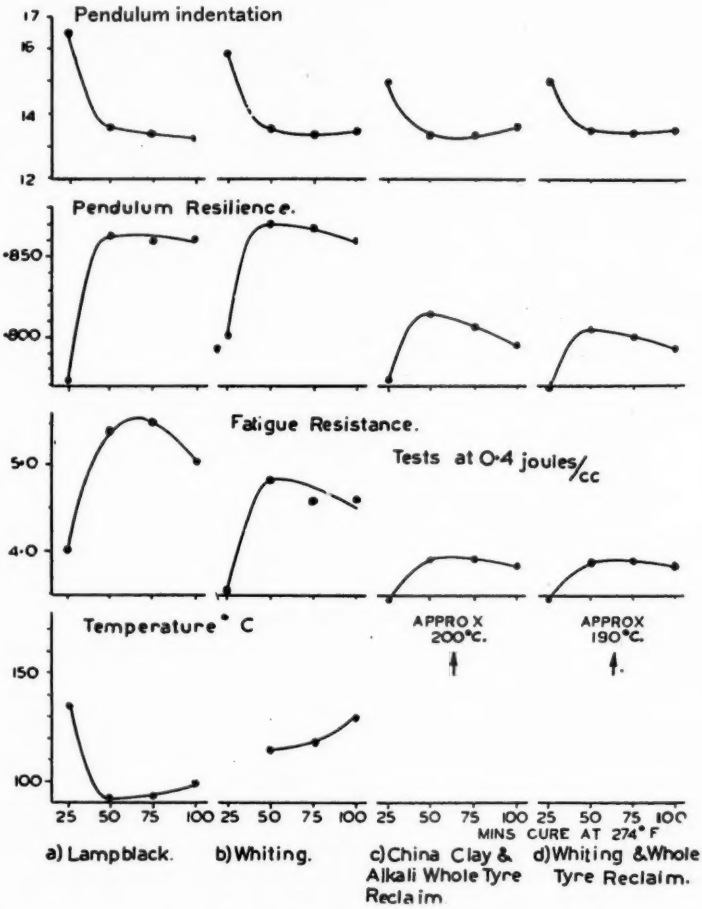


FIG. 26.—Cheap fillers and reclaim.

TABLE XI

REBOUND PROPERTIES OF CARCASS COMPOUND BEFORE AND AFTER FATIGUING

Block before fatiguing	Tripsometer: Indentation	Tripsometer: Resilience (percentage)
Flange	14.1	86.1
Centre	14.6	86.6
Block fatigued at 0.45 joules per cc. after 3000 minutes at 3 cycles per sec.		
Flange	14.1	86.6
Centre	14.6	86.1

a minute and the thermocouple left in the sample the whole time. The curve shows two changes of rates of rise. The first, which will be referred to as the first failing point, appears to coincide with the point where the resilience begins to fall with temperature rise, and the final failing point, which is identifiable with the commencement of a soft porous state of the rubber.

The change in hysteresis characteristics is shown in Table XII, which quotes tripsometer figures on samples taken from different parts of a block of the solid tire compound under consideration which had been run up to the first failing point only.

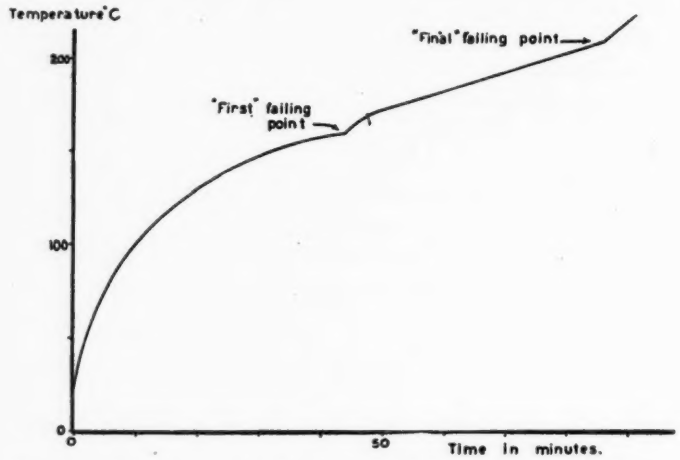


FIG. 27.—Typical temperature-time curve of block tested under conditions to produce an overheating failure.

TABLE XII

HYSTERESIS (REBOUND) PROPERTIES OF SOLID TIRE COMPOUND AFTER FATIGUING

Position of tripsometer sample	Power loss	Indentation	Resilience (percentage)
A—centre of block	44.5	12.15	66.1
B—mid-way between A and C	21.5	9.45	77.2
C—surface of block	18.0	8.70	78.6

(For a definition of "power loss", see Jones and Pearce[13].)

These changes were confirmed by the following tests.

A block showing overheating failing points at 32 minutes (179° C) and 40 minutes (202° C) was retested when cold. It reached 224° C in 18 minutes.

Another block was run up to the first failing point several times, and gave results as shown on Figure 28. The times to this identifiable point are progressively reduced, confirming the tripsometer pendulum data.

Further tests on solid tire compounds show that the hysteresis properties do not exhibit these marked progressive changes at lower temperatures. Several blocks were each run six times to temperatures of 120° C, 130° C and 140° C. When the times of the runs and the times to reach 120° C were examined statistically, it was established that no systematic changes in rates of heating had occurred.

GENERAL CONCLUSIONS

The machine which had been described in the foregoing pages can be used to evaluate fatigue in vulcanized rubber under a variety of stressing conditions, each of which can be accurately controlled. It can be used also to measure heat development and power loss. The stressing conditions used depend on the type of compound under test. Thus solid tire-tread mixings are compared under conditions of constant load and pneumatic tire-casing stocks at constant elastic energy input.

The results of the investigation suggest that fatigue in rubber can be defined as a progressive reduction of strength and resistance to tear resulting from repeated cycles of stress under conditions such that the temperature is kept below

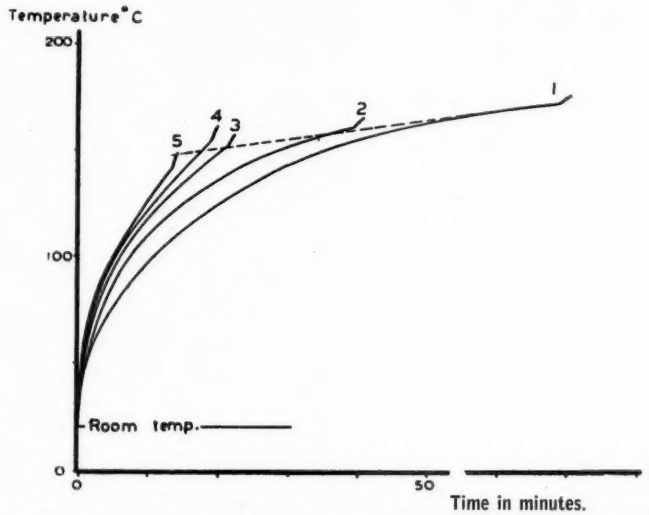


FIG. 28.—Effect of repeated tests to first failing point using same block. (From cold each time.) Curve 1 refers to first test, etc.

the point where hysteresis increases (or resilience falls) with temperature rise. This point varies with the type of compound, being in general lowest in "pure gum" and carcass stocks and highest in pneumatic tread (carbon black) stocks.

During test, the modulus and rate of set vary linearly with the logarithm of the time, and the logarithm of the life is linearly related to the running temperature. For these and other reasons the term, *fatigue resistance,* is defined as the logarithm of the number of blows to failure. If compounds of similar type are being compared, their fatigue properties can often be reasonably assessed, without failure being produced, from considerations of running temperature and rate of set.

The corresponding fatigue resistance at 100° C is a measure of the probable fatigue resistance if the temperature is artificially maintained at 100° C. Its value seems to give an indication of the tear resistance of the compound; this point is receiving further consideration.

In the present paper, modulus is defined as the slope of the line relating actual stress (load divided by deflected cross-sectional area) to actual deflection, and is constant under conditions of pure compression. The research under considera-

tion has shown that the values of the static and dynamic elastic moduli are identical, at least up to 3 cycles per second. The modulus of most compounds which fatigue well increases during the initial temperature rise and continues to increase until failure occurs. Not much work has been done on pneumatic tread compounds, but it has been observed that such compounds tend to soften during test.

The work has shown that raw rubber varies considerably in its capacity to resist fatigue. The causes of this variability have not been fully investigated, but one of them is related to plasticity. In mercaptobenzothiazole-accelerated compounds, initially hard rubbers in general show greater fatigue resistance than highly plastic rubbers, and excessive mastication in any rubber tends to reduce fatigue resistance. Pine tar in moderate quantities can replace mastication with advantage in some types of compound, but used in excess, this softener lowers resistance to fatigue.

Other conclusions reached are that increase of sulfur within limits increases fatigue resistance but reduces tear resistance, that cheap fillers reduce fatigue resistance without necessarily lowering resilience, and that fatigue testing can be used as a means of determining temperature coefficient of vulcanization.

Finally, in the determination of the property which has been defined as fatigue resistance, great accuracy is unattainable. Even with the precise working methods which have been described in this paper, there is still a wide variation in the results obtained.

ACKNOWLEDGMENT

The authors wish to thank the Directors of the Dunlop Rubber Co., Ltd., for permission to publish this paper. They are indebted to several of their present and former colleagues for valuable help, and particularly to J. L. Bloxham, R. F. Hounam and G. F. Payne.

APPENDIX A

Mathematical Theory of Load-measuring Device.—Figure 29 shows a sectional elevation of the load-measuring cylinder, and gives a list of the symbols used below. Figure 30 illustrates the contact lever arm.

Equation of Motion of Piston and its Solution.—A consideration of the forces acting on the piston leads to the following equations:

$$A_1\frac{d^2y}{dt^2}+B\frac{dy}{dt}+Cy=D+E_0.x$$

where $\mathbf{A_1}=\dfrac{W}{g}$ =inertia coefficient.

$B=\dfrac{\eta a}{sg}$ =damping coefficient.

$C=E_0+\dfrac{ae}{T}-\dfrac{A\gamma G}{d}$ =spring coefficient.

$D=W+M+\left(\dfrac{ae}{T}-\dfrac{A\gamma G}{d}\right)y_0-f(H_a)$
=maximum impressed force.

$x=r[\cos(\omega t-\phi)-1]$ =displacement of tool, ignoring effect of obliquity of connecting rod.

$x=0$, $y=0$, at the lowest point of tool and piston motion, respectively.

E_0=stiffness of block under test (*i.e.*, equivalent steel coil spring not the compound modulus).

As B^2-4A_1C is negative the solution of the equation is:

$$y=C_5\varepsilon^{\alpha_3 t}\cos(\beta t+\theta_a)+\frac{D-E_0r}{C}+\sqrt{D_1^2+E_1^2}\cos\left(\omega t-\phi-\tan^{-1}\frac{E_1}{D_1}\right)$$

where natural frequency of oscillation $=\dfrac{\beta}{2\pi}$

$$\alpha_3=\frac{-B}{2A_1};\quad \beta=\sqrt{\frac{C}{A_1}-\left(\frac{B}{2A_1}\right)^2}$$

$$E_1=\frac{\omega BE_0r}{\omega^2B^2+(C-\omega^2A_1)^2};\quad D_1=\frac{(C-\omega^2A_1)E_0r}{\omega^2B^2+(C-\omega^2A_1)^2}$$

$$\frac{E_1}{D_1}=\frac{\omega B}{C-\omega^2A_1};\quad \sqrt{D_1^2+E_1^2}=\frac{E_0r}{\sqrt{\omega^2B^2+(C-\omega^2A_1)^2}}$$

This solution consists of the sum of the displacements due to the natural and forced oscillations of the piston, and some of the cases discussed are illustrated by Figure 31. The constants are evaluated by considering the load on the block at various times.

$$M=E_0\left\{y_0+r-\sqrt{D_1^2+E_1^2}.\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1}\right)+\sqrt{(D_1-r)^2+E_1^2}.\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1-r}\right)\right\}$$

$$C_5=\sqrt{(C_5\cos\theta_a)^2+(C_5\sin\theta_a)^2}\qquad \theta_a=\tan^{-1}\left(\frac{C_5\sin\theta_a}{C_5\cos\theta_a}\right)$$

$$C_5\cos\theta_a=\frac{f(H_a)-W}{C}-\frac{(C-E_0)}{C}\sqrt{D_1^2+E_1^2}.\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1}\right)-\frac{E_0}{C}\sqrt{(D_1-r)^2+E_1^2}.\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1-r}\right)$$

$$C_5\sin\theta_a=\frac{\alpha_3}{\beta}.C_5.\cos\theta_a+\frac{\omega}{\beta}\sqrt{D_1^2+E_1^2}.\cos\left(\phi-\tan^{-1}\frac{D_1}{E_1}\right)$$

When the natural oscillations have been damped out, the equation of motion takes the form:

$$y=\frac{D-E_0r}{C}+\sqrt{D_1^2+E_1^2}.\cos\left(\omega t-\phi-\tan^{-1}\frac{E_1}{D_1}\right)$$

Load Evaluation: General Considerations.—The maximum movement of the piston is given by the condition: $\dfrac{dy}{dt}=0$. The load on the block when the piston is moving is: $Q=M+E_0\ (x-y)$ and is a maximum at $\dfrac{dQ}{dt}=O$. The load

on the block when the piston is stationary is: $Q_{m1}=E_0\ (H-h)$. From a practical standpoint, the relation between this load Q_{m1} and the air pressure value which permits a given piston movement is required.

CASE WHERE CONSTANTS CHANGE IN VALUE AT SOME POINT.—Let the constants change at $t=t_3$, where $y=y_3$. Up to t_3, β, C, D, D_1 and E_1 are applicable. After t_3 up to t_9 β_2, ${}^1C$, ${}^1D$, ${}^1D_1$, and ${}^1E_1$ are applicable. After t_9 the same as up to t_3.

This case occurs in the actual machines, the points t_3 being the point where the piston leaves the permanite washer. And t_9 is the point where the piston recontacts with the washer. For the exact cases, value of y and $\frac{dy}{dt}$ are obtained at t_3, and the values of the new constants C_{15} and θ_2 are obtained from them. The maximum loads, piston movements, etc., are found from the new equations.

SYMBOLS FOR FIGURE 29

A = area of piston.
A_1 = W/g.
$B=\frac{\eta a}{sg}$.
$C=E_0+\frac{ae}{T}-\frac{A\gamma G}{d}$.
${}^1C=E_0-\frac{A\gamma G}{d}$.
$D=W+M+\left(\frac{ae}{T}-\frac{A\gamma G}{d}\right)y_0-f(H_a)$.
E_0 = stiffness of block under test (not modulus of rubber).
G = pressure gauge reading (is negative).
$G_1=\frac{-E_0(H-h)}{A}$.
H_a = atmospheric pressure.
H = initial block height.
M = constant.
$N=\frac{ae}{T}(y_0-y)-AG$.
Q = load on block.
Q_m = maximum load on block during piston oscillation.
Q_{m1} = maximum load during normal running.
Q_n = minimum load during oscillation.
T = thickness of Permanite washer.
T_n = surface tension of oil.
W = weight of piston.
Y_t = piston movement in special case (actual machines).
$a=\pi(r_1^2-r_2^2)$ = area of washer.
d = effective air depth of cylinder.
e = stiffness of washer.
g = 32.2 ft. per second per second.
h = deflected block height.
l_1 = length of piston skirt.
q_1 = oil pressure at r_1.
q_2 = oil pressure at r_2.
r = crank radius.
r_1 = outer washer radius.
r_2 = inner washer radius.
s = radial clearance between piston and cylinder.
t = time from initial contact of tool.
v = velocity of oil.
v_0 = velocity of oil up side of piston.
$x=-r+r\,\mathrm{Cos}\,(\omega t-\phi)$ = tool displacement (zero at lowest point of motion).
y = piston displacement (zero at lowest point of motion).
$y=y_0$ at $t=0$; $y=y_1$ at $t=t_1$, etc.
y_t = total piston movement.
$a=2\pi r_1 l_1$ = area of piston skirt.
$\beta=\sqrt{\frac{C}{A_1}-\left(\frac{B}{2A_1}\right)^2}$ = natural periodicity.
$\alpha_2=-\frac{B}{2A_1}$ = decrement.
η = coefficient of viscosity.
ω = angular velocity of crank.
ϕ = phase angle of crank at $t=0$.
$\gamma=1.41$ = adiabatic constant.
θ_a = phase angle of natural oscillations.
$\epsilon=2.718$.

In the actual machines, the natural oscillations initially set up are negligible at t_3, and it can be shown that under these conditions the following equations are applicable while the piston is clear of the washer.

$$y=C_{15}.\varepsilon^{a_3 t}.\cos(\beta_2 t-\theta_2)+\frac{{}^1D-E_0 r}{{}^1C}+\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}.\cos\left(\omega t-\phi-\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)$$

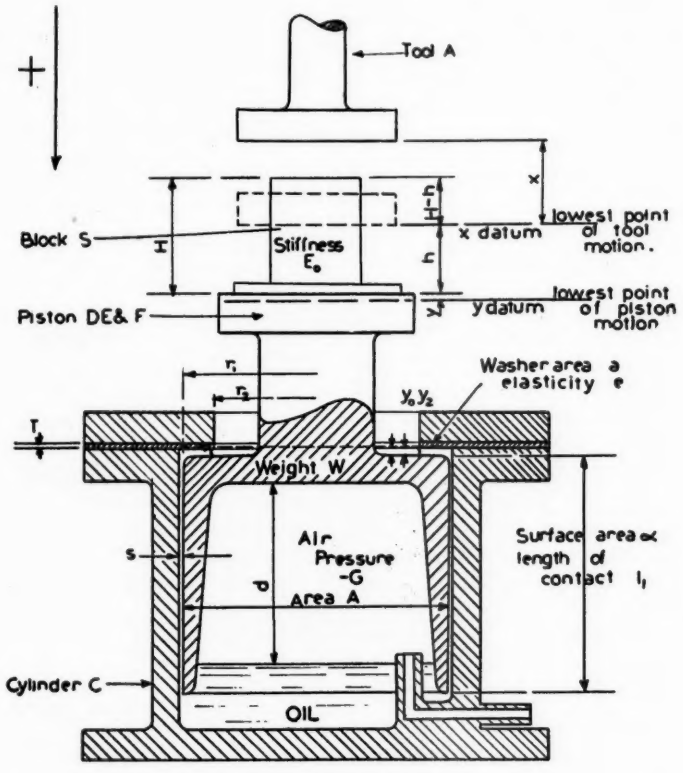


FIG. 29.—Load measuring cylinder.

where θ_2 and C_{15} are complicated functions of practically all the other constants of the motion, and are not included here, as no further use is made of them.

$$t_3 \text{ and } t_9=\frac{1}{\omega}\left\{(\pm)\cos^{-1}\left[\frac{y_2-\dfrac{D-E_0 r}{C}}{\sqrt{D_1{}^2+E_1{}^2}}\right]+\phi+\tan^{-1}\frac{E_1}{D_1}\right\}$$

or in a form of more practical value:

$$t_3 \text{ and } t_9=\frac{1}{\omega}\left\{\phi+\tan^{-1}\left(\frac{{}^1E_1}{{}^1D_1}\right)+(\pm)\cos^{-1}\left[\cos\phi+\left(\frac{-AG-W}{E_0 r}\right)\right]\right\}$$

When the new series of natural oscillations are small enough in amplitude to be neglected, the equation of motion reduces to:

$$y=\frac{{}^1D-E_0r}{{}^1C}+\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}.\cos\left(\omega-\phi-\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)$$

This is identical with the equation which would have been obtained had the motion been calculated from rest (with no washer reaction), using the constants for the second half of the motion (provided the natural oscillations had died out), *i.e.*, the presence of the washer for the first part of the piston's motion serves only to modify the natural oscillations of the second part of the motion and has no effect on the forced oscillation.

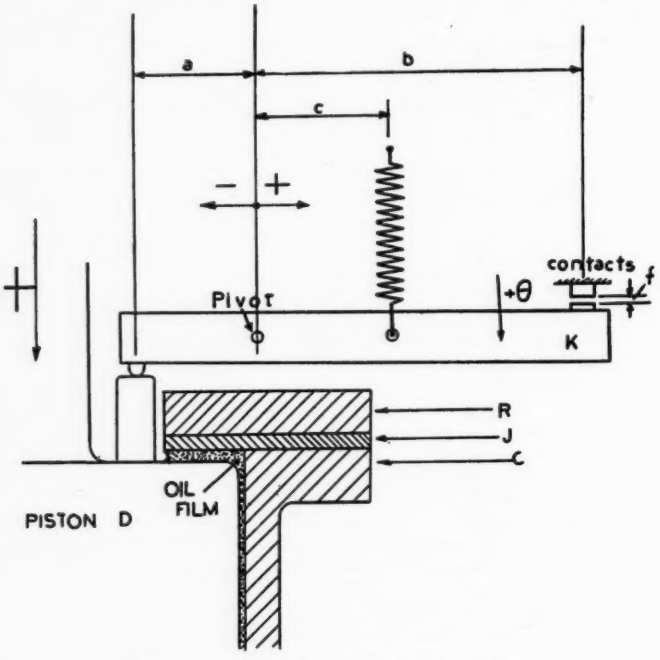


FIG. 30.—Lever contact arm. Load cylinder.

SYMBOLS FOR FIGURE 30

C_n = amplitude constant.
I = moment of inertia of arm around pivot.
K = damping factor.
a_1 = distance from pivot to contact with piston.
b = distance from pivot to electric contacts.
c = distance from pivot to attachment of spring.
d_1 = spring tension.
e_1 = spring stiffness.
f = initial contact gap.
t = time.
u = displacement of arm at point where contacts are mounted.
y = piston displacement.
z = displacement of arm at point where it touches piston.
$f(c)$ = reaction between electric contacts.
$f(z)$ = reaction between arm and piston.
β_1 = natural periodicity of arm.
θ = angular displacement of arm.
$\ddot{\theta}_c$ = critical angular acceleration of arm.
ϕ_1 = phase angle of natural oscillations.

VALUES OF NEW CONSTANTS.—When the piston is not in contact with the washer, the washer reaction is zero, and

$$^1C_1 = E_0 - \frac{A\gamma G}{d}, \quad ^1D_1 = W + M + AG - \frac{A\gamma G}{d} y_0 - f(H_a).$$

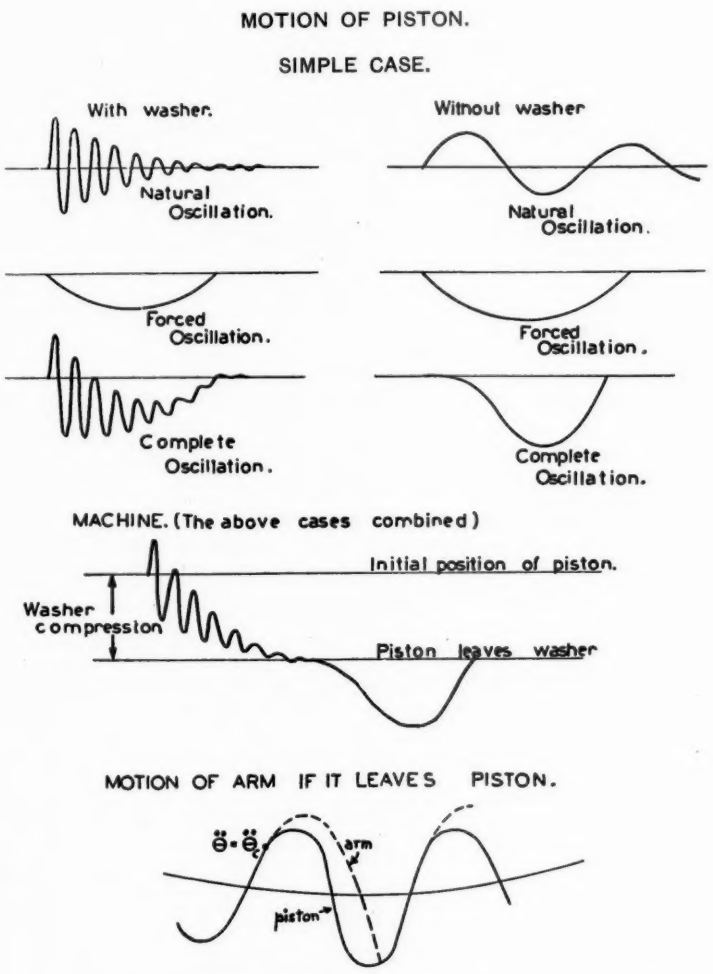


FIG. 31.—Motion of piston as given by theory. Diagrams are not to scale.

When the piston has moved far enough from the washer to break the oil film down, the term $f(H_a)$ is zero. For this to occur, the piston must be at least $\frac{2T_n}{H_a}$ from the washer.

PISTON MOVEMENT (NEGLECTING NATURAL OSCILLATIONS).—Up to the point y_3 at t_3, the piston does not follow the equation of motion obtained using the

constants for the no-washer case, but at the time t_3 has moved an amount y_w=washer compression instead of (y_3-y_0). Let Y_t=total piston movement.

$$Y_t=y_t+y_w-(y_3-y_0)$$

$$y_3=\frac{{}^1D-E_0r}{{}^1C}+\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}.\cos\left(\omega t_3-\phi-\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)$$

$$y_0=C_{15}.\cos\theta_2+\frac{{}^1D-E_0r}{{}^1C}+\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}.\cos\left(\phi+\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)$$

$$Y_t=\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}\left[1-\cos\left(\phi+\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)\right]-C_{15}.\cos\theta_2$$

$$y_t=y_w+\sqrt{{}^1D_1{}^2+{}^1E_1{}^2}\left\{1-\cos\left(\omega t_3-\phi-\tan^{-1}.\frac{{}^1E_1}{{}^1D_1}\right)\right\}$$

The value of the expression in the bracket is obtained from a consideration of the load on the piston as below.

Statically.

At the point B where the washer reaction becomes zero:

$$\left(\frac{H-h}{r}\right)_B=\left(\frac{-AG-W}{E_0r}\right)\text{ for }E_0(H-h)=-AG-W.$$

This corresponds to the crank phase angle of

$$(\omega t_B-\phi)=\cos^{-1}\left[\cos\phi+\left(\frac{-AG-W}{E_0.r}\right)\right].$$

Dynamically.

Owing to the piston inertia and damping, the piston lags behind the tool by $\tan^{-1}\frac{{}^1E_1}{{}^1D_1}$, as shown by expressions for x and y.

The crank position when piston leaves washer is:

$$\phi_2=\omega t_B-\phi+\tan^{-1}\frac{{}^1E_1}{{}^1D_1}=\omega t_3-\phi$$

$$\therefore\left\{1-\cos\left(\omega t_3-\phi-\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right)\right\}=1-\cos\phi-\left(\frac{-AG-W}{E_0r}\right).$$

Hence

$$Y_t=y_w+\frac{W-A(G_1-G)}{\sqrt{\omega^2B^2+({}^1C-\omega^2A_1)^2}}$$

where

$$-AG_1=E_0(H-h).$$

This is the expression used to evaluate the corrections which are applied to the pressure readings.

It also follows that:

$$t_3\text{ and }t_9=\frac{1}{\omega}\left[\phi+\tan^{-1}.\frac{{}^1E_1}{{}^1D_1}+(\pm)\cos^{-1}\left(\cos\phi+\frac{-AG-W}{E_0r}\right)\right]$$

Other special cases have been calculated, but as they cannot be applied for practical reasons, they are not included here.

PISTON ACCELERATION DUE TO FORCED OSCILLATIONS ALONE.—The values of the maximum acceleration of the piston are required for the contact arm theory.

When the piston and washer are in contact, the algebraic maximum acceleration due to the forced oscillation occurs at $t=0$ and is:

$$-\omega^2 \sqrt{D_1^2+E_1^2}.\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1}\right)$$

and its algebraic minimum is $-\omega^2\sqrt{D_1^2+E_1^2}$, which, however, is the maximum numerical value. When the piston and washer are out of contact the expressions are:

$$-\omega^2 \sqrt{{}^1D_1^2+{}^1E_1^2}.\cos\left(\omega t^3-\phi-\tan^{-1}\frac{{}^1E_1}{{}^1D_1}\right) \text{ and } -\omega^2 \sqrt{D_1^2+{}^1E_1^2}$$

respectively

CASE WHERE FORCED OSCILLATIONS CAN BE NEGLECTED.—The piston movement is given by:

$$y_t^1=C_5\left\{\pm\frac{\beta}{\sqrt{\alpha_3^2+\beta^2}}.\varepsilon^{\frac{\alpha_3}{\beta}\left[\theta+\pi/2-\tan^{-1}\frac{\beta}{\alpha_3}+m\pi\right]}.-\cos.\theta_a\right\}$$

where m is an integer and $y^1{}_t$ is the movement corresponding to the $\frac{m}{2}$th oscillation. Maximum movement occurs when m is a minimum and, provided the period of oscillation is small, the movement corresponding to the first oscillation is:

$$C_5\left[\pm\frac{\beta}{\sqrt{\alpha_3^2+\beta^2}}-\cos.\theta_a\right]$$

The load on the block during load measurement oscillates over a range which is approximately given by:

$$\pm\left|\frac{Q_m-Q_n}{2}\right|=\pm\frac{E_0.C_5}{2}\left[\varepsilon.^{\frac{\alpha_3\pi}{\beta}}+1\right]$$
$$\varepsilon^{\frac{\alpha_3}{\beta}\left[\theta-\tan^{-1}\frac{\beta}{\alpha_3}+\frac{\pi}{2}\right]+\frac{\alpha_3\phi}{\omega}}.\cos\left(\frac{\pi}{2}-\tan^{-1}\frac{\beta}{\alpha_3}\right)$$

provided C_5 small.

The piston acceleration varies between the values

$$\pm(\alpha_3^2+\beta^2).C_5.\varepsilon^{\alpha_3 t}.$$

The above expressions have been written for the first part of the motion, but similar expressions apply to the second part of the motion.

GENERAL CASE.—When the frequency of the natural oscillations is large compared with the forced oscillation and the amplitude of the natural oscillation is small, the piston movements, etc., can be considered as the values as given by consideration of the forced oscillations plus a range due to the natural oscillations, each calculated separately as above.

EFFECT OF OIL ON TOP OF PISTON.—If the piston is clear of the oil film on the washer, then the term $f(H_a)$ disappears from the expressions above. In the early testing procedure, this did not hold, hence expressions were obtained in an

attempt to evaluate $f(H_a)$. When the piston is at rest, the force on the piston is $-a\left(H_a-\frac{2T_n}{y_2-y}\right.$ if the oil is just sufficient to maintain a film. If there is a surplus of oil, the force is $-a.H_a$. When the piston is in motion then the force is:

$$f(H_a)=2\pi\left\{\frac{q_2(r_1^2-r_2^2)}{2}-\frac{\eta}{(y-y_2)^2}\left[\frac{dy}{dt}\left(\frac{r_1^4}{4}-\frac{2}{3}r_1^3r_2+\frac{r_1^2r_2^2}{2}-\frac{r_2^4}{12}\right)+2s\,v_0\left(\frac{r_1^3}{3}-\frac{r_1^2r_2}{6}+\frac{r_2^3}{6}\right)\right]\right\}$$

where

$$v_0=\frac{gs^2(G+H_a-q_1)}{4\eta l_1}$$

$$q_1=q_2-\eta\left(\frac{r_1-r_2}{y-y_2}\right)\frac{dy}{dt}+\frac{2\eta v_0 s(r_1-r_2)}{(y-y_0)^2}$$

$q_2=H_a-\frac{2T_n}{y_2-y}$. or H_a, depending on quantity of oil present, and where the piston is moving with a velocity $\frac{dy}{dt}$.

These forces are calculated from the pressures to cause the oil to flow between the piston and washer to maintain a complete oil film and act only over the times during which the oil film is not ruptured.

Their presence would considerably modify the load on the block, but by removing surplus oil and using piston movements greater than $\frac{2T_n}{H_a}$, their effect is zero, except inasmuch as they only produce natural oscillations which are damped out.

Contact Arm Theory.—The piston movements are inferred from the movement of a lever arm which magnifies the piston movement (see Figure 30). The equation of motion of the arm is:

$$\frac{I}{g}\cdot\frac{d^2\theta}{dt^2}+k\frac{d\theta}{dt}=a_1f(z)-c^2\theta e_1+bf(c).$$

When the electric contacts are not touching the last term is zero: .

$$\therefore f(z)=\frac{I}{a_1g}\cdot\frac{d^2\theta}{dt^2}+\frac{K}{a_1}\cdot\frac{d\theta}{dt}+\frac{\theta c^2e_1}{a_1}.$$

In order that the arm and piston shall remain in contact, $f(z)$ must not be negative.

Therefore $\frac{d^2\theta}{dt^2}$ must be algebraically greater than $\ddot{\theta}_c$,

where $$\ddot{\theta}_c=-\frac{Kg}{I}\cdot\frac{d\theta}{dt}-\beta_1{}^2\theta,$$

and where $$\beta_1=c\sqrt{\frac{e_1g}{I}}.$$

Note that this value of $\ddot{\theta}_c$ varies with time.

In general, there are two main classifications.

(*a*) where the angular acceleration algebraically exceeds the critical value at all points in its motion, hence the motion of the contacts is proportional to that of the piston, *i.e.*:

$$\delta u = -\frac{b}{a_1}.\delta z = -\frac{b}{a_1}.\delta y.$$

the previous theory applies without modification;

(*b*) where the angular acceleration is, at some point in the motion of the arm, algebraically less than the corresponding critical acceleration. From this point, the arm leaves the piston, and its motion depends on its own natural constants until such time as it retouches the piston.

Some cases are discussed below.

(i) *General Case.*

At some point $t=t_1(\ddot{\theta}_1-\ddot{\theta}_c)$ is negative, hence $f(z)=0$, and the equation of motion is:

$$\frac{I}{g}\cdot\frac{d^2\theta}{dt^2}+K.\frac{d\theta}{dt}+c^2e_1\theta=0$$

until the arm and piston meet again.

If K is small the equation of motion is:

$$\frac{I}{g}\cdot\frac{d^2\theta}{dt^2}+c^2e_1\theta_1=0.$$

The solution of which is:

$$\theta_1=C_n.\cos(\beta_1 t-\phi_1)$$

Where $\beta_1=c\sqrt{\frac{e_1 g}{I}}$, the natural frequency of oscillation is $\frac{\beta_1}{2\pi}$, and C_n and ϕ_1 are constant.

$$C_n=\sqrt{\theta_1^2+\frac{\dot{\theta}_1^2}{\beta_1^2}}$$

$$\phi_1=\cos^{-1}\left[\frac{\theta_1.\cos\beta_1 t_1-\frac{\dot{\theta}_1}{\beta_1}.\sin\beta_1 t_1}{C_n}\right]$$

The values of θ_1, $\dot{\theta}_1$, $\ddot{\theta}_1$, are being obtained from previous calculations. The point, $(t=t_9)$, where arm and piston retouch is given by finding t_9 where the position of the arm and piston coincide. As the lever cannot reverse its motion under the action of the spring alone over its limited range of movement, at t_9 the lever is at a lowest point in its motion and its position is:

$$z_9=a_1.C_n.\cos(\beta_1 t_9-\phi_1).$$

(ii) *Special Case.*

If the natural oscillations of the piston can be ignored and the arm leaves the piston at $t=0$ and recontacts the instant the contacts close, then:

$$y_t=-\frac{a_1}{b}.u_t+\sqrt{D_1^2+E_1^2}\left\{1-\cos\left[\frac{\omega}{\beta_1}.\cos^{-1}\left(\frac{\theta_0}{\theta_0+\frac{u_t}{b}}\right)-\phi-\tan^{-1}\frac{E_1}{D_1}\right]\right\}$$

In the above case (and it can be shown that the following is also true if piston and arm separate at some time other than $t=0$), y_t lies between $-a_1\frac{u_t}{b}$ and $-\frac{a_1u_t}{b}+2\sqrt{D_1^2+E_1^2}$.

When $\frac{\omega}{\beta_1}$ is small the value of y_t is:

$$-\frac{a_1u_t}{b}+\sqrt{D_1^2+E_1^2}\left\{1-\cos\left(\phi+\tan^{-1}\frac{E_1}{D_1}\right)\right\}.$$

(iii) *Special Case.*

When the frequency of the natural oscillations of the piston is much higher than that of arm, *i.e.*, $\beta>>\beta_1$, the maximum accelerations of the piston due to natural oscillation exceed the critical acceleration in the ratio:

$$\frac{C_5.(\alpha_3^2+\beta^2).\varepsilon^{\alpha_3 t}}{a_1.\ddot{\theta}_c}.$$

If this ratio is high enough, the lever does not follow the natural oscillations but only follows the envelope given by:

$$y^1=\pm C_5.e^{\alpha_3 t}+\frac{D-E_0r}{C}+\sqrt{D_1^2+E_1^2}\cos\left(\omega t-\phi-\tan^{-1}\frac{E_1}{D_1}\right).$$

In the present machines, the negative sign applies as the lever rides on the negative peaks.

CALCULATIONS FOR A TYPICAL CASE.

Constants used.

Machine.

$A=0.1735$ sq. ft. $r=0.125$ ft. $W=29.53$ lbs.
$a=0.0632$ " $d=0.30$ " $\omega=19.5$ radians per sec.
$\alpha=0.468$ " $s=1.9\times10^{-4}$ ft. $\gamma=1.41$

Washer.

$e=2.288\times10^6$ lbs. per sq. ft.
$T=5.21\times10^{-3}$ ft.
$y_w=4.5\times10^{-5}$ ft.

Oil.

At 20° C, $\eta=0.671$.

Block.

$E_0=10{,}000$ lbs. per ft.
$Er=1{,}250$ lbs.
$H=0.246$ ft.
$H-h=0.123$ ft.

$G=-7229$ lbs. per sq. ft.
$\phi=89°\ 5'=1.5548$ radians.
$\cos\phi=0.016$.
$\frac{\phi}{\omega}=0.0797$.
$p=50.2$ lbs. per sq. in.

Contact Arm.

$a=0.0521$ ft.
$b=0.417$ ft.
$c=0.271$ ft.
$W=0.240$ lb.
$\frac{I}{g}=0.00271$ f.p.s. units.

Springs.

$e_1=100$ lbs. per ft. $d_1=2.4$ lbs.

The above data represent the conditions obtaining at the instant of actual load measurement.

The value of E_0 is typical for the mean slope of the load/deflection curves for standard blocks of normal casing compounds.

(*a*) *Motion when Piston and Washer Are in Contact.*

Using the above data it is found that, in the first part of the piston's motion, natural oscillations of frequency of 904 per second and an intial amplitude of 4.3×10^{-6} ft. occur. At the point where piston and washer separate, their amplitude is 1.5×10^{-6} ft. This is sufficiently small to be ignored in deriving the equations of motion for the second part of the piston's motion. The piston leaves the washer at 0.064 seconds after the tool A first touches the block, and the piston has a velocity of 2.7×10^{-4} ft. per second at this point. This is sufficiently low to be ignored when deriving the equations for the second part of the motion.

(*b*) *Motion when Piston and Washer Are Separated.*

In the second part of the movement, the piston's motion is the sum of a forced oscillation and a natural oscillation, the frequency of the latter being 20.5 per second. The velocity corresponding to the forced oscillation at the instant when the piston leaves the washer is 0.58 ft. per second or 2140 times the actual velocity (stated above).

In estimating the effect of the natural oscillation set up, the initial amplitude was calculated on the basis that the piston is at rest when piston and washer separate. This is justifiable in view of the values given above.

The maximum movement when clear of the washer is 2.5×10^{-4} ft. due to the forced oscillation, while the maximum deviation from the forced oscillation path due to the natural oscillation is 6×10^{-5} ft. acting to reduce the piston movement, but not acting in such a manner as to attain its maximum value at the same time as the forced oscillation. Only 0.3 of a complete period of an oscillation at the natural frequency occurs as the piston and washer are separated for only 0.032 seconds (calculated from forced oscillations only). Hence the piston movement has a value between 2.5×10^{-4} ft. and 1.9×10^{-4} ft., and it follows that the total piston movement (including washer) lies between 2.35×10^{-4} and 2.95×10^{-4} ft. This corresponds to a contact gap movement of 0.025 inch if the arm follows the piston without bouncing.

(*c*) *Contact Arm Movement.*

The critical angular acceleration of the contact arm is -100 radians per second^2, which corresponds to a piston acceleration of 5.2 f.p.s.^{2}. The maximum acceleration involved in the forced oscillation is -29.1 ft. per sec. per sec., tending to maintain contact between piston and arm over the whole range of movement encountered. The accelerations involved in the natural oscillation are both positive and negative, and during the period of contact between piston and washer are ± 139 ft. per sec. per sec.; hence the lever follows the envelope of the natural oscillations. When the piston and washer are separated, the maximum accelerations of ± 55 ft. per sec. per sec., due to piston natural oscillations, cause the lever to bounce at its natural frequency of 8.2 vibrations per second. This bouncing reduces the contact arm movement and, without entering into very complex calculations, its must be assumed that the arm follows a path intermediate between the forced oscillation and the envelope of the natural oscilla-

tions superimposed on the forced oscillation. Hence it is sufficiently accurate to assume that the whole of the contact arm movement of 0.025 inch is due to the forced oscillation of the piston and that the clicks in the 'phone would cease at the gauge pressure of 50.2 lbs. per sq. in., the pressure given in the original conditions above and from which the amplitude of the forced oscillation has been calculated.

(*d*) *Load on Block.*

The actual load on the block when the piston is at rest is 1230 lbs. or 49.2 lbs. gauge. Hence 1.0 lb. per sq. in. must be deducted from the gauge reading to obtain the true load. While the actual movement is in progress, the load does not exceed 1207 lbs. (48.3 gauge) due to the forced oscillation alone, and the range of load variation due to natural oscillations of the piston is rather less than 14 lbs. (0.5 gauge).

(*e*) *Effect of Oil on Top of the Piston.*

With typical piston velocities, and very small movements (2×10^{-5} ft.), such as were used in the early methods of test, forces whose theoretical magnitude are of the order of 10^6 lbs. can exist; of course the actual forces do not attain these values, owing to change of conditions, but the calculations show that large errors are involved if an oil film is present during the operation of load measurement.

The use of a piston movement of $2.6 \times^{-4}$ ft. (present standard method) is sufficient to break down the oil film; this is confirmed by Figure 32, which shows that the gauge readings measured with rising and falling pressures are the same at this movement.

Diagrams obtained from Machine.—The motions of the piston and punching tool were also investigated from a practical standpoint by attaching styles so that they traced lines on a uniformly revolving smoked drum. The traces obtained indicated that the theory outlined above is substantially correct. A record of the piston oscillations when the piston and washer were in contact was not obtained because of the small amplitude of the motion and the relatively low natural period of the style.

The motion of the piston when clear of the washer can be clearly resolved into the sum of a forced oscillation and a damped natural oscillation, the period of the latter being of the same order as that given by calculation. It should be noted that records were obtained with larger piston movements than usual, but they show that the natural oscillations are small compared with the forced oscillations. Figure 33 confirms the curves in Figure 31, which are deduced from the theory.

Application of Theory.—The following procedure is now standard practice:

(1) A contact gap of 0.025 inch, and the free oil on the piston top removed before it accumulates.

(2) The mean of the readings with rising and falling pressures is taken as the gauge reading, and a correction is applied to obtain the true load.

(3) The spring on the contact arm is sufficiently stiff to ensure that the arm follows the forced oscillation of the piston.

The actual value of the contact gap is a compromise depending on the following factors:

(1) The movement is sufficient to break down the oil film between piston and washer; this results in equal gauge readings with rising and falling pressures.

(2) The movement is not so great that the pressure fluctuations due to piston movement are sufficient to cause oscillations of the gauge pointer.

(3) The movement is not so large that it exceeds the smallest adjustment normally made to the deflection of a block during a test; otherwise the corrections involved would be too large for satisfactory results.

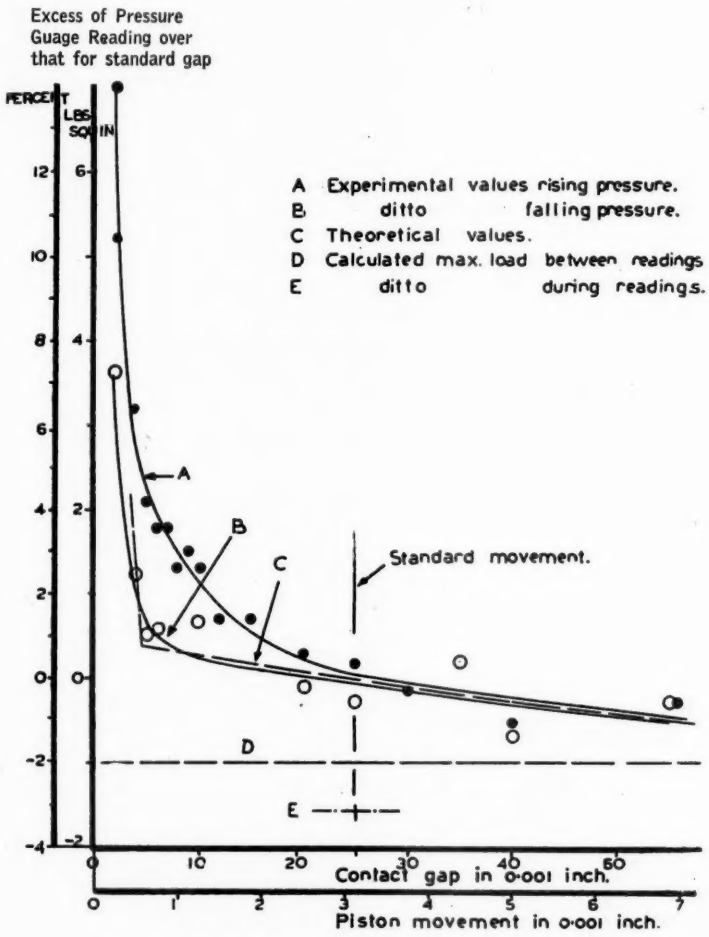


FIG. 32.—Effect of piston movement on pressure gauge reading.

(4) Nor is the movement so large that the accelerations necessitate an exceedingly strong spring to cause the lever arm to follow the piston.

A further consideration also arises; the permanite washer must be in such a state that the assumptions involved in calculating the corrections are justified, *i.e.*, it must not be in a state of partial failure. The washers fail around the top edge of the piston and do not leak air and oil until some time after the failure commences. This point is covered by the weekly check tests.

Evaluation of Corrections for Maximum Load.—The method adopted to determine the correction to be applied to the gauge reading is to plot the piston movement for various gauge pressures and to find the pressure which allows the standard movement.

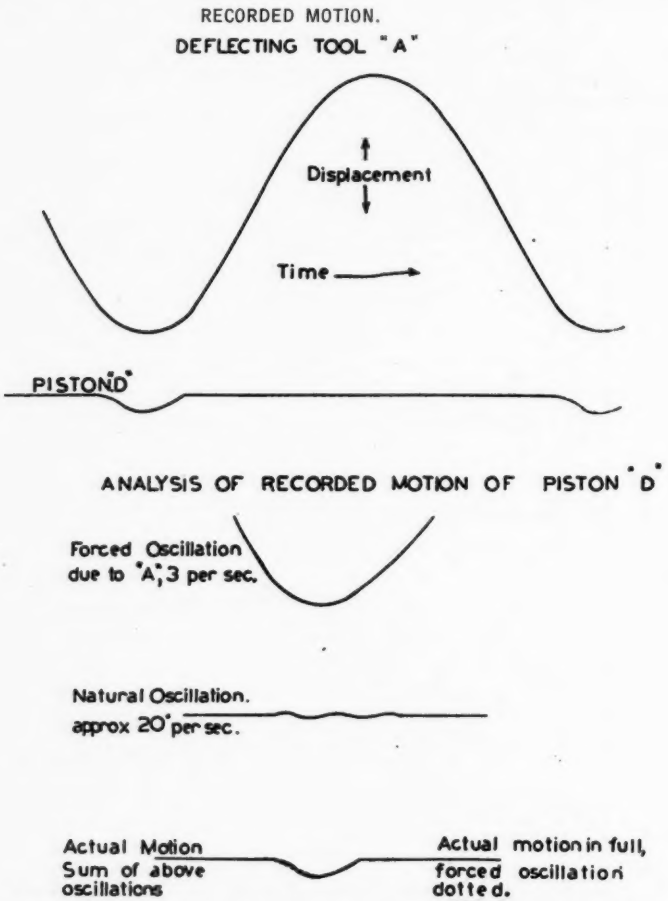


Fig. 33.—Analysis of observed piston motion. Diagrams reproduced to scale.

For blocks and test conditions within the following ranges:

Speed of machine, 180 to 192 r.p.m.
Pressure gauge reading between 40 and 60 lbs. per sq. in.
Deffected height between 35 and 40 mm.
Work input between 0.45 and 0.55 joules per cc.
Oil levels and pipe lengths remaining unaltered (and as at present).
Room temperature 20° C.

The correction is 1.0 lb. per sq. in. to be subtracted from the gauge reading.

Reference to Figure 32 shows that smaller contact gaps would not only require larger corrections but also introduce a large uncertainty into the value.

APPENDIX B

ERRORS.—Mean errors are used rather than standard errors (which equal 1.25 mean errors), as they are easier to calculate and are sufficiently precise.

Pressure Gauges.

These are standard gauges made by the Budenburg Gauge Co., and are marked to 1.0 lb. per sq. in. By a comparison between the two gauges and a mercury manometer, the error is found to be below 0.1 lb. per sq. in. The readings are estimated to 0.1 lb. per sq. in., and the corrected pressures are considered to be within ±0.5 per cent.

Height Gauges.

The scale and vernier are marked to 0.02 mm. As a result of detailed experimental work, it has been shown that the mean error of estimated block height is ±0.05 mm., and the maximum error encountered once only in any one test is

TABLE XIII

MEAN ERRORS IN HEIGHT READINGS DUE TO STATED CAUSES

(These were measured with vernier reading to 0.01 mm. over a large number of readings)

Cause	Amount (mm.)	Symbol
Insensitiveness of feeler	±0.02	F
Wrong location of click in 'phones	±0.01	t
Inaccuracy of assumed feeler thickness	±0.01	Z
Inaccuracy of assumed height of standard	±0.01	p
Inaccuracy of zero correction	±0.03	g

±0.2 mm. From calculations of the form outlined below, it follows that the mean error on the estimated percentage deflection is ±0.05 per cent, and the maximum error occurring once per test is of the order of 0.2 per cent.

It was shown also that a maximum error of slightly less than four times the mean error occurs less than once in 20 readings (the usual span of a test).

Let a be the error in the top of the undeflected block.
b the error in the top of the deflected block.
c the error in the zero correction.
d the measured free height.
e the measured deflection.

Then from the theory of errors the true free height:

$$H=d\pm\sqrt{a^2+c^2}.$$

Where $a^2=F^2+t^2+z^2$

$b^2=t^2$

$c^2=t^2+g^2=p^2+3t^2$.

$$\text{True deflection}=D=\frac{e\pm a\mp b}{d\pm a\mp c}=\frac{e}{d}\left[1\pm\sqrt{a^2\left[\frac{d-e}{ed}\right]^2+\frac{b^2}{e^2}+\frac{c^2}{d^2}}\right]$$

Input Work Errors.

If the load/deflection relations are correct, the height and pressure reading errors give a mean error of 0.2 per cent for the work input readings, with a maximum error of 0.9 per cent about once per test. An analysis of the load/deflection data shows the maximum errors in the derived laws to be less than 3 per cent. Although this results in a possible maximum error of 4 per cent, the maximum error involved in using the law to make adjustments is only ± 1.0 per cent. The corresponding means errors are ± 1.0 per cent and ± 0.3 per cent per reading. The errors in machine adjustment are small. Ignoring the first hour, as the block properties are rapidly changing and more frequent adjustment is made, it can be shown that the estimated average work input for each one-half hour period is within ± 1.0 per cent of the required value. Over the whole test, the work input is within 0.5 per cent of the required value or, allowing for errors of measurement, within ± 1.5 per cent of the absolute value.

Modulus.

The errors in modulus are of the same order as those of the work.

Temperature.

The cold couple is known to within 0.5 C degrees, the needle calibration to 1.0 C degrees, and the block temperatures are probably within ± 1.5 C degrees on each reading. The room temperature varies around a constant value, with a mean deviation of the average daily temperature of ± 0.6 C degrees, and this produces a mean error of ± 0.8 C degrees in the mean running temperature.

Speed.

The instantaneous value of speed can be read to ± 0.5 r.p.m., or ± 0.25 per cent. Due to fluctuations of mains, voltage etc., it is impossible to maintain constant speed without continual adjustment. In spite of this, unattended machines are usually within 2 per cent of the correct stroboscope speed, and it follows that the recorded average value of the speed over a test is within ± 1 r.p.m., or ± 0.5 per cent, even in extreme cases. This means that the mean speed quoted for the test is within ± 1 per cent of its true value.

Estimation of Point of Failure.

The point of failure is estimated between two readings 30 minutes apart; hence, assuming that the state of the failed block helps in the estimation of the time to failure, a mean error of 15 minutes is obtained. On a block of fatigue resistance 5.0, this is a change of 0.02 in the value.

Effect of Work Input, Temperature, Speed and Point of Failure on Fatigue Resistance.

Using the above values and fatigue resistance temperature data and, in the absence of exact relationships, assuming that variations in work input and speed cause the same percentage change in fatigue resistance, it can be shown that the above mean errors, together with a mean error of 1.0 C degree in the daily room temperature, result in a mean error of 1.5 per cent in the estimated fatigue resistance.

Weekly Check Tests.

To maintain the present degree of accuracy, it is considered advisable to carry out weekly check tests with a view to discovering any errors as they may arise.

The following are the items which are subjected to check tests, together with the maximum ranges of variation encountered over the two machines under normal conditions:

Height gauge correction (compared with standard)...	± 0.05 mm.
Pressure gauges—direct comparison.....	± 0.1 lb. per sq. in.

A block is interchanged between the two machines

Block loads are within.....	± 0.2 lb. per sq. in.
Temperatures are within.....	± 1 C degree.

provided speed and deflections are accurately maintained.

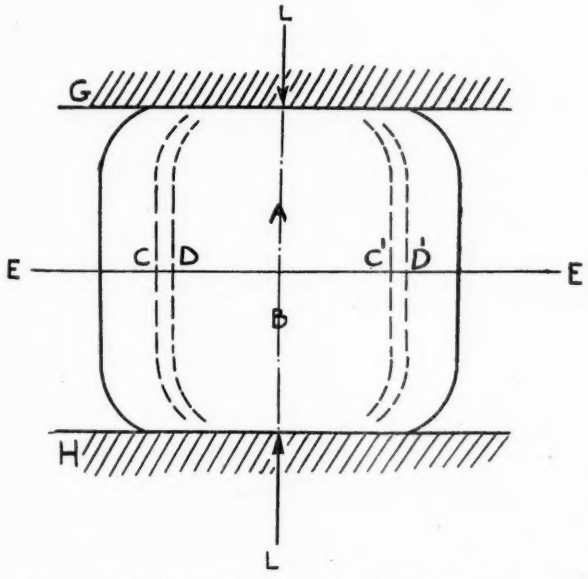


FIG. 34.—Illustrating the proof of the statement that the stress within the parallel part of a compressed cylinder is uniform and purely compressive. See Appendix C.

If variation occurs outside these limits, the matter is investigated. This weekly check is useful particularly in indicating when an old washer (load measuring device) is causing unreliable results, as without some similar check the washer would commence to fail and adversely affect results for some time before it failed to act as an effective air seal.

APPENDIX C

UNIFORMITY OF COMPRESSIVE STRESS WITHIN BLOCK.—Consider a cylindrical block compressed between two platens G and H (see Figure 34). Let EE be the midplane of the block, A the upper half and B the lower half. The stress distribution in B must be a "mirror image" of that in A. This follows from the symmetry of the block.

As no concentrated external load is actually applied to the equatorial plane EE, the lines of principal stress cutting this plane cannot be discontinuous; therefore these lines are perpendicular to plane EE. It follows from the properties of the lines of principal stress that there is no shear in plane EE at any point. Consider now a thin cylindrical shell CD C′D′. There is no shear across the annular cross-section, and as a shear is always accompanied by a shear of equal value in a plane at right angles to itself, no shear exists between the outer face of the shell CD′ and the inner face DC′. Absence of shear between these two faces necessitates equality of the compressive stresses on the plane EE inside the thin shell and those on the plane outside the shell. As the shell considered is arbitrarily chosen, the stress (direct compressive) across plane EE is uniform. No shear stress exists on the midplane EE for the following supplementary reason: if shear did exist, there would be a resultant radially outward force due to each half A and B, which would be additive and would not be in equilibrium. The uniformity of stress on plane EE applies to all blocks. In the case of compressed blocks below the critical deflection, where a parallel cylindrical portion exists, it follows also that the compressive stress must be uniform within that parallel part. Confirmation of this is found in a comparison of blocks of various heights under the same load, for in all cases where a parallel part exists, the deflected diameter is the same.

It follows also that the stress within the "end caps" is complex, and involves shears. A further consequence is that the stress within a block above the critical deflection (that is, no parallel part under load) is complex, except at the midplane.

It should be noted that this reasoning is general, and is not restricted to any particular stress-strain relationship of the material.

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ANALYTICAL METHODS IN RUBBER CHEMISTRY

PART V

ESTIMATION OF THE OXYGEN OF HIGHLY AUTOÖXIDIZED RUBBER CONTAINED IN CARBOXYL, ESTER, CARBONYL, EPOXIDE AND HYDROXYL GROUPS *

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In the course of a study of the autoöxidation of natural rubber and of low-molecular olefins of allied structure, it has been necessary to ascertain the nature and relative proportions of the functional groups to which the ingoing oxygen may give rise. Up to the present it has been established[1] that the products of autoöxidation reactions are in general highly complex mixtures, and that even such simple olefins as dihydromyrcene and cyclohexene may give rise to molecules which bear a varied assortment of hydroperoxide, alcoholic hydroxyl, epoxide and carbonyl groups. Available evidence further indicates that the primary products of autoöxidation are hydroperoxides, formed by the reaction of oxygen at methylene groups adjacent to double bonds, and that it is the secondary reactions which these hydroperoxides undergo which are responsible, directly or indirectly, for the formation of the other oxygen-containing groups which have been observed. Molecules of rubber hydrocarbon contain, on an average, several thousand methylene groups adjacent to double bonds. Each such methylene group is at least the potential seat of oxidative attack, and it might be anticipated that if the autoöxidation of rubber proceeds in a manner analogous to that of simpler olefins, the products of reaction would be extremely complex and that they might contain any or all of the following functional groups: (1) olefin $=C=C=$ (2) hydroperoxide $\equiv C.O.O.H$, (3) Alcohol $\equiv C.OH$, (4) carbonyl .CHO, (7) epoxide $=\overset{|\frown|}{C.O.C}=$ and (8) ether $\equiv C.O.C\equiv$. The proportion of any one present is, however, likely to vary considerably with the experimental conditions during and subsequent to the oxidation.

The existence of considerable residual unsaturation in oxidized rubbers is already known, and it is determinable with reasonable accuracy by the iodine value method of Kemp, Bishop and Lasselle[2]. The total content of hydroxylic oxygen, including that present in hydroperoxide groups, can be estimated with some precision in such nonvolatile, high-molecular substances as modified rubbers by an adaptation of the Zerewitinoff method for the determination of active hydrogen[3], while the oxygen bound in peroxide groups can be estimated separately by a colorimetric method which depends in principle on the oxidation by peroxide of colorless ferrous thiocyanate to red ferric thiocyanate[4].

Although it touches on the estimation of active hydrogen and of peroxide oxygen, the present communication is concerned more particularly with a first attack on the complicated problem of bringing to analysis those portions of oxygen in highly oxidized rubbers which are contained in carboxyl, ester, car-

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bonyl and epoxide groups. The numerical results obtained and set out below are to be regarded as approximations to the true values, and they can be valid only if the assumptions detailed in the text are valid. In the absence of absolute methods of checking, confirmatory evidence can come only in the course of further experimental work.

The oxidized rubber.—The material selected as the subject of analysis was an extensively oxidized rubber which is commercially available under the trade name of Rubbone-B, and which comprises that fraction of Rubbone (a product obtained by prolonged mastication of rubber in the presence of air, cobalt naphthenate and cellulosic material[5]) which is soluble in acetone but insoluble in methylated spirits. Rubbone-B has an oxygen content of 11 to 12 per cent, the exact value depending somewhat on the conditions under which it has been prepared. It is believed that the material is as complex in constitution as any oxidized rubber which is likely to be encountered, although unlike some oxidized rubbers, it contains only a very low percentage of peroxidic oxygen.

Estimation of peroxidic oxygen.—The oxygen bound in peroxide groups, as estimated by the method of Bolland *et al.* (*loc. cit.*), amounted in two specimens of Rubbone-B to less than 1 per cent of the total oxygen present. This somewhat low value is not wholly unexpected, since Rubbone-B, both during its preparation and isolation, is subjected for considerable periods to temperatures ranging from 70° to 120°, and under such temperature conditions the somewhat thermolabile hydroperoxide groups could not be expected to survive in appreciable quantities.

Estimation of hydroxyl oxygen.—The active hydrogen content of one specimen of Rubbone-B, as determined by the method of Bolland[3], was equivalent to 3.5 per cent of hydroxylic oxygen, *i. e.*, 31 per cent of the total oxygen. This hydroxyl oxygen represents the sum of the oxygen bound in alcoholic hydroxyl groups, and in enolized ketone groups, plus one-half the oxygen present in carboxyl and in hydroperoxide groups.

Estimation of carboxyl oxygen.—The acidity of the material was determined by direct titration with standard alkali. Both carboxyl and hydroperoxide groups exhibit an acid reaction, but only a negligible proportion of observed acidity can be accounted for in terms of the latter grouping, even if it is assumed that the peroxide oxygen is wholly contained in hydroperoxide groups. It may, therefore, be concluded that the acidity of Rubbone-B is due to the presence of free carboxyl groups, and that each carboxyl group requires one equivalent of alkali for neutralization. On this basis the acidity of two specimens of the material corresponded to the presence of 0.4 and 0.3, respectively, of carboxyl oxygen, *i.e.*, 3 to 4 per cent of the total oxygen.

Estimation of ester groups.—When determining the acidity of Rubbone-B, it was observed that the end-points of the titration faded with unexpected rapidity, and this observation suggested that the material contained functional groups which were attacked by free alkali. This indication was confirmed when estimations of the saponification value were made[6], for it was then found that the total quantity of alkakli consumed in reaction both with ester groups and with free carboxyl groups amounted to some five or six times the amount required to neutralize the free acidity only.

For two separate specimens of Rubbone-B, the ester oxygen was found to amount to 2.0 per cent and 1.6 per cent, *i.e.*, to 14 to 18 per cent of the total oxygen present.

Concerning the way in which the oxidation of rubber gives rise to esterified carboxyl groups, nothing is known with certainty. It is, however, conjectured

that they may be formed by interaction of hydroxyl and of epoxide groups with carboxyl groups, and that the latter arise mainly by reactions involving oxidative scission of the carbon chains. The possible mechanism of such scission reactions is discussed below, in connection with the mode of formation of carbonyl groups.

The estimation of carbonyl (ketone and aldehyde) oxygen.—The analytical procedure which has been adopted for the estimation of aldehyde and ketone oxygen is based in principle on the capacity of the carbonyl group in ketones and aldehydes to react with aluminium isopropylate, according to the equation:

$$R_1R_2.CO + (CH_3)_2CHOal \rightleftarrows R_1R_2CH(Oal) + (CH_3)_2CO \quad \ldots\ldots (1)$$

$$\left(al = \frac{Al}{3} \right)$$

The reaction is one which is specific for aldehydes and ketones, and by employing an excess of aluminium isopropylate and distilling off the acetone continuously as it is formed, the reaction can be forced towards completion[7].

On the assumption that each atom of carbonyl oxygen which is reduced gives rise to one molecule of acetone, it is possible, by estimating the quantity of acetone produced, to measure the quantity of aldehyde or ketone oxygen contained in the material under reduction.

With regard to the efficiency of aluminium isopropylate as a reducing agent, data available indicate that under conditions comparable to those employed in the present estimations, reduction usually proceeds to an extent greater than 80 per cent and frequently passes 90 per cent[7]. It must, however, be borne in mind that carbonyl groups in terpenoid compounds of even moderately high molecular weight may exhibit a somewhat depressed reactivity towards the usual reagents for this grouping[8].

For two separate specimens of Rubbone-B, the oxygen found in aldehyde and ketone groups amounted to 0.4 per cent and 0.7 per cent, *i.e.*, to 3 to 7 per cent of the total oxygen. The mode of reaction by which these groups arise has not been established, but it is readily conceivable that they owe their formation to a process of oxidative scission of the rubber chains, according to the equation:

$$(.CH_2C(CH_3):CH.CH_2)_n + nO_2 \longrightarrow nCH_2.\dot{C}(CH_3):O + nCH_2.CHO \quad \ldots\ldots (2)$$

Under the somewhat drastic conditions employed in the preparation of Rubbone-B, aldehyde groups would almost certainly suffer further oxidation to carboxyl groups and, in consequence, it is not improbable that ketonic oxygen predominates in proportion over aldehydic oxygen.

Estimation of epoxide oxygen.—Although an analytical method exists for estimating the simple epoxide compound, ethylene oxide[9], no general procedure for the estimation of epoxide groups is known; indeed, in fact, the chemical behavior of even the simple olefine oxides has been but superficially investigated.

It would, however, appear that all of the reagents known to undergo reaction with epoxides[10] may also undergo reaction with at least one other of the oxygen-containing functional groups which have been already enumerated. That is to say, a wholly selective analytical reagent is not available. Of the reagents of limited selectivity, one class was considered to possess potential analytical utility, namely, secondary aliphatic amines. It has been shown[11] that such amines react with epoxides according to the equation:

$$=C.\overset{|\text{———}|}{O}.C= + R_2NH \longrightarrow =C(NR_2).C(OH)= \quad \ldots\ldots (3)$$

the reaction being catalyzed by water. These observations have been extended by Horne and Shriner[12] for the reaction between diethylamine and ethylene oxide, and from their work it is evident that this reaction proceeds mainly in the sense of Equation (3), although products corresponding to the addition of further molecules of ethylene oxide at the hydroxyl group of the tertiary amino-alcohol were observed to be formed in minor quantities, and in proportions depending on the conditions of reaction.

Before attempting to apply the reactivity of aliphatic secondary amines to the estimation of epoxide groups in oxidized rubber, the utility of the principle involved was examined with respect to the estimation of the epoxide oxygen content of two simple oxirane derivatives, cyclohexene oxide and isobutylene oxide. Known masses of these compounds were treated with excess of diethylamine in the presence of water, and the extent to which the reaction proceeded was estimated by determining the amount of tertiary amino compound formed in accordance with Equation (3). From this quantity, the amount of epoxide oxygen which had reacted could be calculated, and hence the epoxide-oxygen content of the samples taken for analysis. In this way it was found that the overall errors involved in the estimation of the epoxide-oxygen contents of cyclohexene oxide and of isobutylene oxide did not exceed 10 per cent of the true values, and in general were somewhat less.

In extending the principle of the analytical procedure to the estimation of the epoxide-oxygen contained in Rubbone-B, it had to be borne in mind that aliphatic secondary amines, such as diethylamine, may enter into reaction not only with epoxide groups, but also with carboxyl, with ester and with carbonyl groups. The reaction of secondary amines with carboxyl groups give rise to substituted ammonium salts and to N-disubstituted amides:

$$.CO.OH + R_2NH \begin{cases} \rightarrow .CO.ONH_2R_2 \\ \rightarrow .CO.NR_2 + H_2O \end{cases} \quad \ldots\ldots\ldots\ldots (4)$$

while esters and lactones in reacting with secondary bases suffer cleavage to compounds containing *N*-disubstituted amide groups and hydroxyl groups:

$$.CO.OR + R_2NH \rightarrow .CO.NR_2 + R.OH \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Nonconjugated carbonyl groups do not, in general, react additively with secondary amines, but it is to be noted that aldehydes or ketones containing nonconjugated carbonyl groups may, under the influence of bases, condense to form conjugated compounds thus:

$$=CO + CH_2 \cdot CO \rightarrow =C:\dot{C}.CO. + H_2O \quad \ldots\ldots\ldots\ldots\ldots (6)$$

and that these conjugated compounds may then undergo an addition reaction of the type:

$$=C:\dot{C}.CO. + R_2NH \rightarrow R_2NC.CH.CO. \quad \ldots\ldots\ldots\ldots\ldots (7)$$

In submitting Rubbone-B to analysis for epoxide oxygen, the material was heated in the absence of air with diethylamine and a small amount of water, and the total quantity of nitrogen which had entered into combination determined. Now this quantity of nitrogen may have entered into the reaction product as the result of any or all of the reactions expressed by Equations 3, 4, 5, and 7, and it is not possible to determine directly what proportion is present as the result of the addition of diethylamine to epoxide groups (Equation 3). It is,

however, possible to estimate the quantity of nitrogen present in the form of substituted amides and of ammonium salts by hydrolyzing the reaction product with phosphoric acid. The difference between the total nitrogen and the hydrolyzable nitrogen then affords a measure of that nitrogen, assumed to be unhydrolyzable, which has combined with the Rubbone-B as the result of the reaction of diethylamine with epoxide groups (Equation 3) and carbonyl groups (Equation 7).

For one sample of Rubbone-B, the experiments established the presence of a nominal 0.5 per cent of epoxide oxygen, a quantity equivalent to 4 per cent of the total oxygen present. However, as indicated above, some unknown proportion of this four per cent may be present in the form of carbonyl groups.

Analyzed and unanalyzed oxygen.—The results of the foregoing analyses are summarized below.

Nature of oxygen-containing functional group	Oxygen present, expressed as percentage of total oxygen	
	Preparation 1 (Samples 1 to 3)	Preparation 2 (Sample 4)
Peroxide	1	1
Hydroxyl	31	—
Carboxyl	4	3
Ester	18	14
Carbonyl	4	7
Epoxide (plus carbonyl)	4	—

They account for 50 to 60 per cent of the total oxygen in Rubbone-B, and there thus remains some 40 to 50 per cent of oxygen which has not been brought to analysis. The form in which this unanalyzed oxygen is present is not known, but it seems probable that it is bound largely in ether groups (for the estimation of which no direct method yet exists), and perhaps to some small extent in epoxide groups of abnormally low reactivity. Indeed, it seems quite likely that, under the conditions employed in the preparation of Rubbone-B, ether groups would arise as the result of the interaction of epoxide and hydroxyl groups:

$$=\overset{|}{\underset{|}{\overbrace{\underset{|}{\overset{|}{C}}.O.\underset{|}{\overset{|}{C}}}}}= + \equiv C.OH \rightarrow \equiv C.O.\breve{C}\ .\ \breve{C}(OH) \qquad (8)$$

EXPERIMENTAL

Isolation of Rubbone-B from commercial Rubbone.—Rubbone (100 g.) was heated 1 hour under reflux with industrial methylated spirits (100 cc.). The mixture was allowed to cool to room temperature, the alcoholic extract decanted and the alcohol-insoluble portion further extracted with methylated spirits (50 cc.). The combined alcoholic extracts, which contained Rubbone-C, were rejected.

The residue remaining after extraction by alcohol was refluxed for 0.5 hour with acetone (150 cc.) and the mixture allowed to cool to room temperature. The resultant suspension was subjected to prolonged centrifuging, by which it was, however, not completely clarified. The somewhat cloudy acetone extract was decanted, and the acetone-insoluble material again extracted with acetone (50 cc.). The acetone-insoluble Rubbone-A was rejected, and the acetone solution containing Rubbone-B was concentrated on a water bath, at first at atmospheric pressure, and finally *in vacuo*.

Drying of Rubbone-B for analysis.—An attempt was made to dry to constant weight samples of Rubbone-B destined for analysis. The use of elevated temperatures, *e.g.*, 70°, for this purpose is not desirable, as it brings about a gelling

which is probably accompanied by chemical changes. In a preliminary experiment, a sample of the material contained in a highly-evacuated glass tube, to which was attached a side-tube cooled in liquid air, was maintained at 40° for 36 hours and then at room temperature for 12 hours. During this treatment volatile substances were evolved continuously, and further attempts to dry the sample to constant weight were abandoned.

The decision was made to work with a product which had been dried to an arbitrary although fairly thorough extent. To accomplish the requisite drying, 20-30 grams was placed in a glass tube 15 × 3 cm., one end of which was closed and the other fitted with a ground-glass joint. The tube was attached via a liquid air trap and a tap to a high-vacuum line; it was inclined at an angle of 10° to 20° to the horizontal, and by rotating it about the ground joint, the viscous Rubbone-B could be caused to flow under gravity and so to expose fresh surfaces to the high vacuum. Drying was continued 4 to 8 days, and the material was thereafter stored at atmospheric pressure under oxygen-free nitrogen.

Elementary analyses of Rubbone-B.—Two preparations of Rubbone-B were made from the same large-scale batch of Rubbone. The analyses for samples 1 to 3 below relate to materials drawn from the first preparation which were dried *in vacuo* to arbitrary and somewhat different extents. Sample 4 was drawn from the product of the second separation. The three analyses are for samples taken from different parts of the same dried viscous mass. The values are percentages.

Sample 1. C, 77.8; H, 10.6; N, 0.1; 0 (diff), 11.5.
Sample 2. C, 78.1; H, 10.7; N, 0.1; 0 (diff), 11.1.
Sample 3. C, 77.9; H, 10.4; N, 0.1; 0 (diff), 10.9.
Sample 4. C, 78.4; H, 10.5; N. 0.2; 0 (diff), 10.9. C, 78.5; H, 10.5; N, 0.2; 0 (diff), 10.8. C, 78.8; H, 10.5; N, 0.2; 0 (diff), 10.5.

Estimation of peroxide oxygen.—The peroxide content of Rubbone-B was estimated by the method of Bolland, Sundralingam, Sutton and Tristram.

Sample 1. *Found:* 0.03, 0.04 per cent peroxide oxygen. *Sample* 4. *Found:* 0.008, 0.006 per cent peroxide oxygen.

Estimation of hydroxyl oxygen.—The active hydrogen content of Rubbone-B was estimated by the modified Zerewitinoff method of Bolland, Sundralingam, Sutton and Tristram[4]. The quantity of hydroxyl oxygen present was calculated on the assumption that the active hydrogen was present wholly in combination with hydroxyl groups.

Sample 1. *Found:* 6.7 mg., 13.4 mg. gave respectively 330, 660 cu. mm. of CH_4 at N.T.P. Hence the quantity of oxygen present in hydroxyl groups was 3.5 and 3.5 per cent.

Determination of the acid value of Rubbone-B.—Portions (*ca.* 1 g.) of the material were weighed into flat-bottomed glass tubes (2 × 1 cm.), dropped into benzene (25 cc., Analar grade) or freshly-distilled dioxane (25 cc., British Drug Houses, Ltd., "highly-purified"), and the mixture was warmed to 30° to 40° in nitrogen to hasten dissolution. When benzene had been employed as a solvent, absolute alcohol (25 cc.) was added after dissolution was complete. The solution was cooled to room temperature, and titrated with standard 0.1 *N* aqueous baryta or 0.5 *N* aqueous sodium hydroxide solution, using phenolphthalein as an internal indicator. The end points of the titration were somewhat obscured by the brown color of Rubbone-B. Blank titrations were carried out in order that allowance might be made for the acidity of the solvents. It was observed that,

when titrating Rubbone-B samples, the end points faded more rapidly than when titrating blank solutions.

Sample 1. *Found:* Acid no. 6.2, 8.6, 6.4, calculated to be equivalent to 0.35, 0.49, 0.36 per cent, respectively, of carboxyl oxygen.

Sample 4. *Found:* Acid no. 6.1, 4.7, calculated to be equivalent to 0.35, 0.26 per cent, respectively, of carboxyl oxygen.

DETERMINATION OF THE SAPONIFICATION VALUE OF RUBBONE-B.—Portions of the material (*ca.* 1 g.) were weighed into flat-bottomed glass test tubes. Each portion was then dropped into a flask fitted with a gas-inlet tube reaching to the bottom, and a reflux condenser surmounted by a gas outlet tube which dipped a few mm. below the surface of a light lubricating oil. Nitrogen, purified according to the procedure of Fieser[13], was passed through the inlet tube to displace air and the sample was taken up in benzene (25 cc., Analar grade) or in freshly distilled dioxane (25 cc., British Drug Houses, Ltd., "highly-purified"). A definite volume (25 cc.) of 0.1 *N* alcoholic potash was added to the solution, and the mixture heated under reflux in nitrogen for the desired period. The contents of the flask were then cooled to room temperature, diluted freely with boiled-out distilled water, and titrated with standardized 0.1 *N* sulfuric acid, using phenolphthalein as indicator. The end points of the titrations were somewhat obscured by the brown color of Rubbone-B. Control experiments in which the Rubbone-B was omitted were carried out under identical conditions, thus permitting a correction to be applied for the quantity of alkali consumed by reaction other than saponification.

Sample 1. *Found:* Saponification values, 44, 41, calculated to be equivalent to 2.5, and 2.3 per cent of oxygen, bound in free and in esterified carboxyl groups. The oxygen bound in esterified carboxyl groups = (2.4−0.4) per cent = 2.0 per cent.

Sample 4. *Found:* Saponification value (3 hrs.) 30, 32; (6 hrs.) 31, 31; equivalent to 1.7, 1.8; 1.7, 1.8 per cent, respectively, of oxygen bound in free and in esterified carboxyl groups. The oxygen bound in esterified carboxyl groups = (1.8−0.3) per cent = 1.5 per cent.

ESTIMATION OF OXYGEN BOUND IN ALDEHYDE AND KETONE GROUPS.—*Apparatus.*—This comprised a flask (50 cc.), to which was sealed, a short distance below the neck, a gas inlet tube of capillary bore. The neck of the flask carried a Vigreux column having an indented section 15 × 1 cm., and the column-head was fitted with a thermometer and an outlet tube for vapors. Over this outlet tube was slipped a small condenser jacket. The condensed vapors passed into a trap (15 × 2 cm.), cooled in ice. This in turn was connected to a similar trap cooled in liquid air, the exit tube from which dipped a few millimeters below the surface of oil contained in a boiling tube. Connection between the various parts of the apparatus was made by means of ground-glass joints.

Reagents. Toluene (British Drug Houses, Ltd., sulfur-free) was distilled immediately before use, and the foreruns containing water were rejected. Isopropyl alcohol was dried by refluxing over quicklime, and then twice distilled through a short column, the second distillation being carried out over 2,4-dinitrophenylhydrazine. A middle cut boiling over a 1° range was taken.

Aluminum isopropylate was prepared in isopropyl alcohol solution by the procedure described by Lund[7]. Dry toluene was added to the solution, and unreacted isopropyl alcohol distilled off. The solution of aluminum isopropylate in toluene remaining in the flask was diluted with additional toluene to the desired

concentration. The reagent employed in the experiments described below contained, in 70 cc. of toluene, 2.2 g. of aluminum as aluminum isopropylate.

2,4-Dinitrophenylhydrazine solution.—This was prepared by dissolving 1 g. of the solid in 50 cc. of concentrated hydrochloric acid and diluting with water to 300 cc. The reagent was filtered immediately before use.

Procedure.—The whole apparatus was cleaned by a nitric acid-chromic acid mixture, soaked in distilled water and thoroughly dried in an oven at 110°. The Rubbone-B (*ca.* 1 g.) was accurately weighed into a flat-bottomed glass test tube (2 × 1 cm.), dropped into the flask fitted with a side-arm, and toluene (25 cc.) and a small piece of porous pot added. The apparatus was assembled, the ground-glass joint connecting the flask with the fractionating column being lubricated by a toluene-insoluble citric acid—tetramethylene glycol condensation product[14]. Nitrogen which had been freed from oxygen by passage through Fieser's solution[13] and dried by concentrated sulfuric acid was passed in through the side-arm on the reaction flask, and when the air had been displaced from the apparatus, the contents of the flask were warmed on a water bath to 30 to 40°, and shaken from time to time to aid dissolution of the Rubbone-B. When dissolution was complete (0.5-0.75 hour) the contents of the flask were cooled in ice, the fractionating column was momentarily detached, and aluminum isopropylate solution (10 cc.), followed by isopropyl alcohol (5 cc.), added. The quantity of aluminum isopropylate employed was five times in excess of that which would be theoretically required to reduce all the oxygen present if it were combined in the form of aldehyde or ketone groups.

The fractionating column was replaced, passage through the apparatus of a slow stream of nitrogen (*ca.* 1 bubble in 2 sec.) begun, the trap nearest the reaction flask surrounded by crushed ice, and the other trap was cooled in liquid air. The flask was placed in an oil-bath, the temperature of which was maintained at 60° to 70°, and raised at hourly intervals to 110° to 120° for 3 to 5 minutes, so that 1 to 2 cc. of isopropyl alcohol, and with it any acetone formed in the reaction, were driven over. After 4 to 5 hours' heating, the contents of the reaction flask were cooled in ice, the traps allowed to warm up to room temperature, and their contents washed out with 5-10 cc. of distilled water. The traps were then replaced, a further quantity (5 cc.) of isopropyl alcohol was run into the flask, and the heating, etc., carried out as before.

In 8-10 hours, when reduction had proceeded largely towards completion, the contents of the flask were cooled to room temperature, and the apparatus, through which nitrogen passed continuously, allowed to stand overnight. Next morning a further quantity of isopropyl alcohol (5 cc.) was run into the flask, and reduction proceeded with as on the previous day. It was ascertained, by testing the contents of the traps for acetone, that the reaction was complete in 15-18 hours.

The liquid rinsed out of the traps was a mixture of water, acetone, toluene and isopropyl alcohol. To extract the acetone, the mixture was shaken with an equal volume of water, the resultant emulsion centrifuged, the aqueous layer separated from the toluene, and the extraction repeated until the aqueous extract no longer gave a precipitate when tested with a few drops of 2,4-dinitrophenylhydrazine hydrochloride solution.

The aqueous extracts were bulked and treated with an excess of the 2,4-dinitrophenylhydrazine hydrochloride reagent. The precipitate of insoluble acetone-2,4 dinitrophenylhydrazone was filtered off on a weighed sintered-glass Gooch crucible (No. 4 porosity) washed with cold water and dried to constant weight *in vacuo* over phosphorous pentoxide. In order that due allowance might

be made for any 2,4-dinitrophenylhydrazone formed from any aldehydes or ketones present in the reagents, or in the Rubbone-B, a control experiment was carried out under identical conditions, aluminum isopropylate being omitted. The quantity of 2,4-dinitrophenylhydrazone obtained in such experiments never exceeded 5 per cent by weight of that isolated in the determinations proper, and in general it amounted to much less.

Sample 3. *Found:* 0.93 g. gave 54 mg. of acetone-2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with authentic acetone-2,4-dinitrophenylhydrazone, 125°. In the control experiment, less than 0.0 mg. of this derivative were obtained. Percentage of aldehyde- or ketone-oxygen in sample $(16.0 \times 0.054 \times 100) \div (238.1 \times 0.93) = 0.4$ per cent.

Sample 4. *Found:* Aldehyde or ketone oxygen 0.80, 0.65, 0.74.

Note on the estimation of acetone.—Although it has been stated in the literature that 2,4-dinitrophenylhydrazine can be employed as a reagent for the quantitative estimation of acetone[15], no details are available concerning the accuracy with which the estimations can be made.

Experiments were accordingly carried out on the precipitation from aqueous solution of known amounts of acetone, using quantities of the order of those encountered in connection with the above reductions with aluminum isopropylate, *i.e., ca.* 10 mg. acetone.

Found: 9.64, 9.64, mg. acetone. *Required:* 10.07 mg. acetone. Hence the error was 4 per cent.

ESTIMATION OF OXYGEN BOUND IN EPOXIDE GROUPS.—*Reaction of diethylamine with cyclohexene oxide and with isobutylene oxide.*—Cyclohexene oxide was synthesized from cyclohexene[16]. Cyclohexene (123 g.) afforded, on treatment with hypochlorous acid, 2-chlorocyclohexanol, b.p. 79°/24 mm. (53 g.). The 2-chlorocyclohexanol was stirred with caustic soda solution, the product worked up, and the cyclohexene oxide twice distilled through a 20 × 1 cm. adiabatic column of the partial-reflux type, packed with $\frac{3}{16}$ inch single-turn glass helices. A middle fraction (18 g.) of b.p. 129° to 130° was collected separately, and employed in the experiments described below.

Isobutylene oxide was synthesized from isobutylene by a procedure which followed closely that described by Wilson and Lucas[17] for butylene oxide.

Isobutylene chlorohydrin was prepared as follows. A solution of hypochlorous acid was prepared by passing chlorine into a solution of mercuric chloride (25 g.) and caustic soda (190 g.) in water (100 g.) containing ice (800 g.)[18]. The solution was placed in a 3-necked flask with a bell-stirrer and a gas inlet tube, the end of the latter being so placed that gas bubbling into the solution was sucked into the interior of the stirrer, whence it emerged in the form of fine bubbles. Isobutylene was passed into the solution until all the hypochlorous acid had reacted. The solution was steam-distilled, and the distillate worked up to give isobutylene chlorohydrin, b.p. 126° to 128°/746 mm. (30 g.).

To prepare isobutylene oxide, isobutylene chlorohydrin (30 g.) was dropped into a stirred solution of sodium hydroxide (75 g.) in water (38 g.) which was maintained at 90° to 95°, and the isobutylene oxide distilled off continuously as formed[17]. The crude oxide (21.5 g.) was fractionated through a column containing a section (10 × 1 cm.) packed with $\frac{3}{16}$ inch single-turn glass helices. A fraction b.p. 49° to 49.5° was collected for use.

Reagents. Diethylamine (British Drug Houses, Ltd.) was redistilled over caustic soda immediately before use, and a middle fraction boiling over less than

a 1° range was collected. Ether was stored over sodium and distilled before use. The benzene (Analar) and toluene were distilled before use.

Reaction procedure.—Spherical thin-walled glass bulbs (*ca.* 1 cm. diam.) were blown on the end of thin capillary tubes, weighed, filled with olefin oxide, sealed and reweighed. One or more of the bulbs, containing in all *ca.* 1 g. of oxide, was placed together with a piece of glass rod (2 to 3 cm. long) in a thick-walled glass pressure tube. The tube was drawn out to a thick-walled constriction, and diethylamine (10 cc.), together with water, introduced through the constriction by means of a long-stemmed glass funnel. The contents of the tube were chilled in liquid air[19], the funnel was withdrawn from the constriction and was replaced by a gas inlet tube through which nitrogen was passed. It was observed that, if air were not displaced from the tube, the subsequent heating yielded products which were badly discolored and which contained tarry material. The pressure-tube was sealed off at the constriction while the current of nitrogen was still passing. It was heated at 140° to 150°, allowed to cool, and the contents were rinsed with ether into a flask. The unreacted diethylamine was distilled off on a

TABLE I

Expt.	Olefin	Temp.	Time (hrs.)	Water added (percentage *)	Extent of reaction (determined by titration)	Extent of reaction (determined by Kjeldahl N)
1	Cyclohexene Oxide	140°–150°	48	25	68	66
2		"	"	65	96	94
3		"	"	91	97	94
4	Isobutylene Oxide	"	"	65	95	90
5		"	"	51	94	92
6	Cyclohexene Oxide	110°	16	0	14	—
7		140°	26	0	23	—
8	Isobutylene Oxide	110°	14	0	4	—
9		140°	26	0	15	—

* Expressed as a percentage of the mass of olefin oxide.

water bath through a Vigreux column, and benzene added to the residue. The benzene was distilled off through a column of the partial reflux type, distillation being continued until the distillate no longer contained diethylamine.

The residue in the flask was taken up in alcohol or in water, and titrated with *N* sulfuric acid, using methyl red as an internal indicator. The neutralized solution was made strongly acid with concentrated hydrochloric acid, transferred to a Kjeldahl flask, and evaporated to dryness on a steam bath. The nitrogen in the residue was estimated by a Kjeldahl macroprocedure.

Effect of water on the extent of reaction.—Experiments were carried out with reaction mixtures containing constant quantities of olefin oxide and of diethylamine and varying amounts of water. The results are given in Table I.

In the absence of added water (Expts. 6 to 9), reaction proceeded only to a small and somewhat variable extent. As the quantity of water was increased, the reaction proceeded further towards completion (Expts. 1 and 2) and the addition of 65 per cent of water was sufficient to ensure that 90 per cent or more of the olefin oxides entered into combination with diethylamine (Expts. 2 to 5).

Reaction of diethylamine with Rubbone-B.—A sample (*ca.* 1 g.) of dried Rubbone-B was weighed into a flat-bottomed glass tube (2 × 1 cm.) and introduced into a glass pressure tube (60 × 2 cm.). A ground-glass joint was sealed to the open end of the pressure tube, and below this open end a thick-walled

capillary constriction was made. Toluene (10 cc.), and diethylamine (10 cc.) containing the requisite amount of water, were introduced through a long-stemmed glass funnel passing through the constriction. The pressure tube was then attached to a liquid-air trap, which in turn communicated via a tap to a Pirani gauge and a 2-stage oil diffusion pump. The trap and the contents of the tube were cooled in liquid air, and the apparatus was evacuated to about 0.1 mm. The tap was closed, the trap and the frozen contents of the tube were allowed to warm to room temperature. The tube and the trap were again cooled in liquid air and the tap was then opened; the gas which had become disengaged from the liquid was pumped off until the residual pressure was about 0.01 mm. This cycle of operations was repeated three to four times, until the final residual pressure of air was 10^{-3} to 10^{-4} mm. While in communication with the pump, the tube was sealed off at the constriction and transferred to a tube furnace, in which it was heated at 140° to 150°. The tube was allowed to cool, the contents washed into a flask, and the unreacted diethylamine distilled off *in vacuo* from a water bath. To remove the last traces of diethylamine from the residue, the flask was highly evacuated, maintained at 30° to 40°, and left for 30 to 40 hours in connection with a side tube immersed in liquid air.

The nitrogen in the residue remaining in the flask was determined by a Kjeldahl semimicro method[20]. The material proved to be unusually resistant to digestion by sulfuric acid, and it was necessary, when employing selenium as a catalyst, to allow digestion periods of 120-150 hours.

The influence of water on the extent of reaction between diethylamine and Rubbone-B.—Experiments were carried out to ascertain the quantity of water which it was necessary to add to catalyze, to the maximum extent, the reaction between diethylamine and any epoxide groups in Rubbone-B. In these experiments, which were carried out according to the procedure described above, the same amounts of toluene, diethylamine and Rubbone-B were employed, but the quantity of water added was varied. The reaction mixture was heated at 140° to 150° for 100 hours, the Rubbone-B—diethylamine reaction product worked up, and analyzed for nitrogen. *Found:* N (Expt. 1, using 28 per cent H_2O) 0.85 per cent; N (Expt. 2, using 59 per cent H_2O) 0.83 per cent; N (Expt. 3, using 98 per cent H_2O) 0.84 per cent.

(*Note.*—The mass of water added and the mass of nitrogen in the reaction product are in each case expressed as percentages of the mass (*ca.* 1 g.) of Rubbone-B employed).

The quantity of nitrogen entering into the product was thus not increased by employing more than 30 per cent of water. It was frequently observed that the presence of 60 to 100 per cent of water in the reaction mixtures resulted in the formation of gelatinous insoluble material, so that the use of more than 30 per cent of water appeared to be not only unnecessary, but possibly undesirable.

Influence of reaction time on the extent of reaction between diethylamine and Rubbone-B.—Experiments were carried out in which the quantities of diethylamine, toluene, Rubbone-B (sample 2), and water (*ca.* 30 per cent by weight of the Rubbone-B were heated together at 140° to 150° for different times, and the quantity of nitrogen present in on the products estimated. *Found:* for reaction product after 100 hours, N 0.80, 0.78 per cent (Expts. 4 and 5; for reaction product after 150 hours, N, 0.90, 0.93 per cent (Expts. 6 and 7). Thus, extension of the time of reaction from 100 hours to 150 hours brought about some increase in the extent of reaction.

Hydrolysis of Rubbone-B-diethylamine products.—The Rubbone-B-diethylamine reaction product, prepared under the conditions employed in Expts. 6 and 7, was dissolved in dioxane (10 cc.) and the solution transferred to a pressure tube which had been drawn out to a capillary constriction at a short distance below the open end. To the dioxane solution were added an excess of syrupy phosphoric acid (d. 1.75, 0.6 cc.), water (0.1 cc.) followed by dioxane (10 cc.)[21]. The tube was sealed at the constriction and heated at 140°. It was allowed to cool and the contents, which remained homogeneous, were transferred to a Kjeldahl distillation apparatus of the semimicro type, using dioxane as a wash liquid. The dioxane solution was made alkaline with aqueous sodium hydroxide solution (15 cc., 50 per cent), and steam-distilled, the distillate being caught in 0.1 N sulfuric acid solution (25 cc.). The acid consumed was estimated by titration with 0.1 *N* aqueous sodium hydroxide solution. Blank experiments (8 and 9) were carried out to ascertain the quantity of volatile nitrogen to which the reagents and the nitrogenous groups originally in the Rubbone-B might give rise. The following data were obtained, the times shown relating to hours of heating with phosphoric acid, and the nitrogen split off expressed as a percentage of the mass of the Rubbone-B from which the material submitted to reaction with phosphoric acid was derived. *Found:* N (for 25-hour reaction period, Expts. 8 and 9) 0.01 per cent; 0.01 per cent; N (for 34-hour period, Expt. 10), 0.41 per cent; N (for 49-hour period, Expt. 11), 0.32 per cent.

Thus the extent of hydrolysis was not increased by increasing the reaction period from 34 hours (Expt. 10) to 49 hours (Expt. 11).

Evaluation of the quantity of oxygen bound in epoxide and in α, β-unsaturated carbonyl groups.—The average nitrogen content of a product of 150 hours' reaction period was 0.92 per cent (Expts. 6, 7), and the average quantity of nitrogen split off by hydrolysis was 0.36 per cent (Expts. 8 to 11). The Rubbone-B contained, before treatment with diethylamine −0.12 per cent of nitrogen, only 0.01 per cent of this being, however, hydrolyzable (Expts. 8 and 9). Assuming that (0.12−0.01) per cent of nitrogen remained in an unhydrolyzable form after treatment with diethylamine, the unhydrolyzable nitrogen to which reaction with diethylamine gave rise amounted to 0.92—(0.36+0.11)=0.45 per cent. If it is assumed that this unhydrolyzed nitrogen is bound in tertiary amino groups which have arisen by the addition of diethylamine at epoxide groups or at double bonds conjugated to carbonyl groups, then it is equivalent to $0.45\times16/14=0.5$ per cent of epoxide plus α, β-unsaturated carbonyl oxygen.

The carbon and hydrogen microanalyses were carried out by W. T. Chambers. The author is greatly indebted to E. H. Farmer for much helpful advice and criticism.

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RUBBER ANALYSIS OF PLANTS IN SOUTH CAROLINA *

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In 1930 and 1931 some plants growing in the vicinity of Clemson, South Carolina, were collected and analyzed for the presence of rubber. The plants were collected and identified by M. A. Rice, the chemical tests being made by the other two authors. The results are presented below. The figures given at the right show the percentage of rubber in each case. All determinations were made on a basis of air-dry weight.

Name of plant	Percentage
Ambrosia trifida L. Great ragweed	0.27
Amsonia Tabernaemontana Walt. Amsonia	0.26
Apocynum cannabinum L. Indian hemp	
No. 9: leaves	1.16
No. 17:	0.73
Asclepias tuberosa L. Butterfly weed	
No. 5: stems	0.34
leaves	2.20
No. 18:	2.21
No. 22:	1.80
Asclepias sp. Milkweed	
No. 7: stems	0.38
leaves	1.93
No. 10:	1.55
Asimina triloba Dunal. Papaw	0.54
Aster sp. Wild aster	1.03
Broussonetia papyrifera (L.) Vent. Paper mulberry	0.60
Cacalia atriplicifolia L. Pale Indian plantain	1.75
Decumaria barbara L. American decumaria	0.08
Erigeron annuus (L.) Pers. White-top	
Stems	0.09
Leaves	0.69
Eupatorium purpureum L. Joe-pye weed	0.45
Euphorbia corollata L. Flowering spurge	
Stems	0.26
Leaves	0.53
Euphorbia nutans Lag. Spotted spurge	0.26
Euphorbia sp. Spurge	0.70
Helianthus atrorubens L. Purple-disk sunflower	0.68
Lactuca sagittifolia Ell. Arrow-leaved lettuce	0.20
Lactuca Scariola L. Prickly lettuce	
No. 44	0.43
No. 45	0.34
Lonicera japonica Thumb. Japanese honeysuckle	0.50
Morus rubra L. Red mulberry	1.02
Oxydendrum arboreum (L.) DC. Sourwood	0.24
Parthenium integrifolium L. American fever-few	1.05
Passiflora incarnata L. Maypop	0.25
Pyrrhopappus carolinianus (Walt.) DC. False dandelion	
No. 1: whole plant	0.51
No. 2: stems	0.45
leaves	0.60
roots	0.61

* Reprinted from *Science*, Vol. 95, No. 2477, pages 624-625, June 19, 1942.

Name of plant	Percentage
Rhus glabra L. Smooth sumach	
Stems	0.38
Leaves	0.30
Robinia hispida L. Rose acacia	
Stems	0.29
Leaves	0.44
Sambucus canadensis L. Common elder	1.27
Silphium compositum Michx. Rosin-weed	0.74
Smilax sp. Greenbrier. (Material from a correspondent)	
No. 39: flesh of berries	1.85
No. 41: flesh of berries	3.65
No. 42: flesh of berries	2.05
Solidago spp. Goldenrod	
No. 3: stems	0.12
leaves	0.69
No. 12: whole plant	0.89
No. 23:	1.33
No. 24:	1.45
Tephrosia virginiana (L.) Pers. Cat-gut	0.23
Verbesina occidentalis (L.) Walt. Small yellow crownbeard	1.22
Vinca minor L. Periwinkle	0.97
Vincetoxicum carolinense (Jacq.) Britton. Vincetoixcum	2.09

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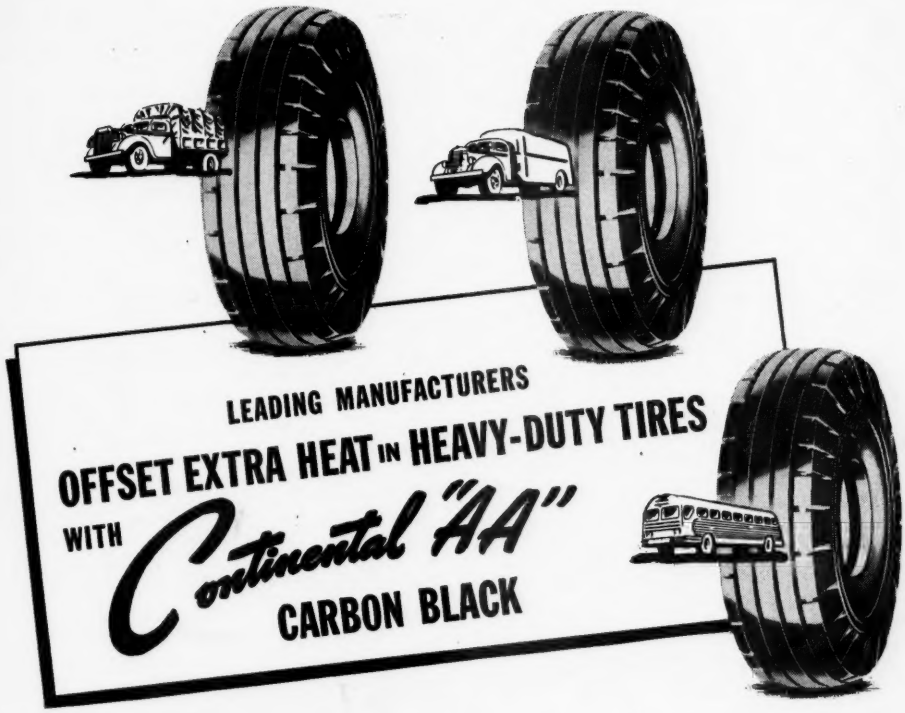

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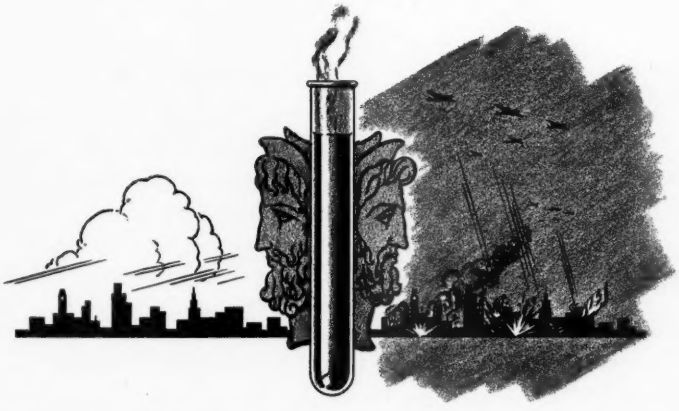

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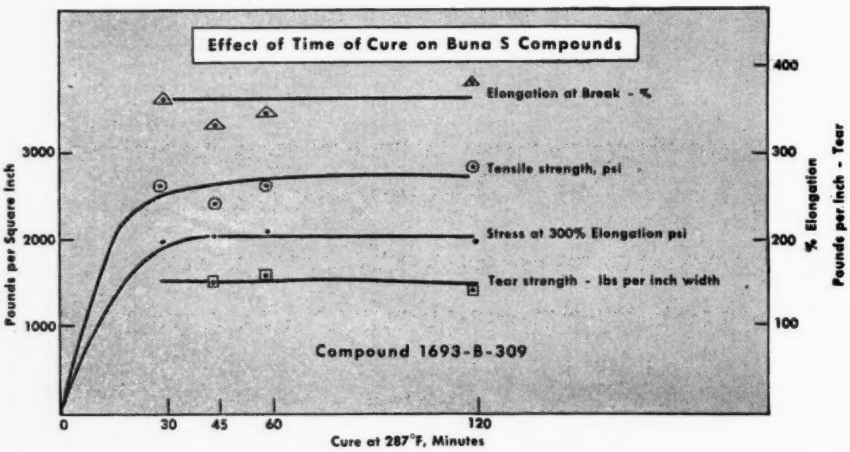

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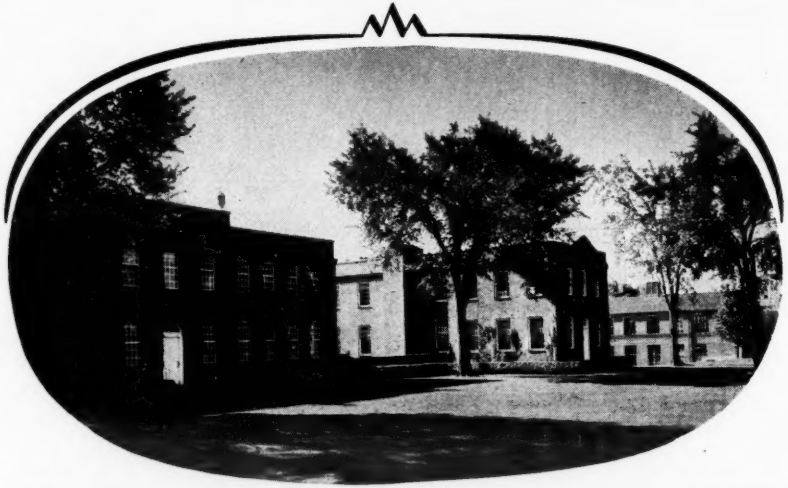

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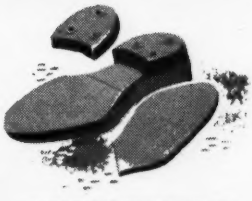

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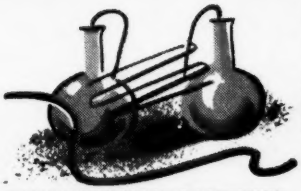

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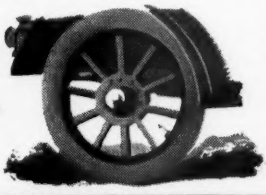

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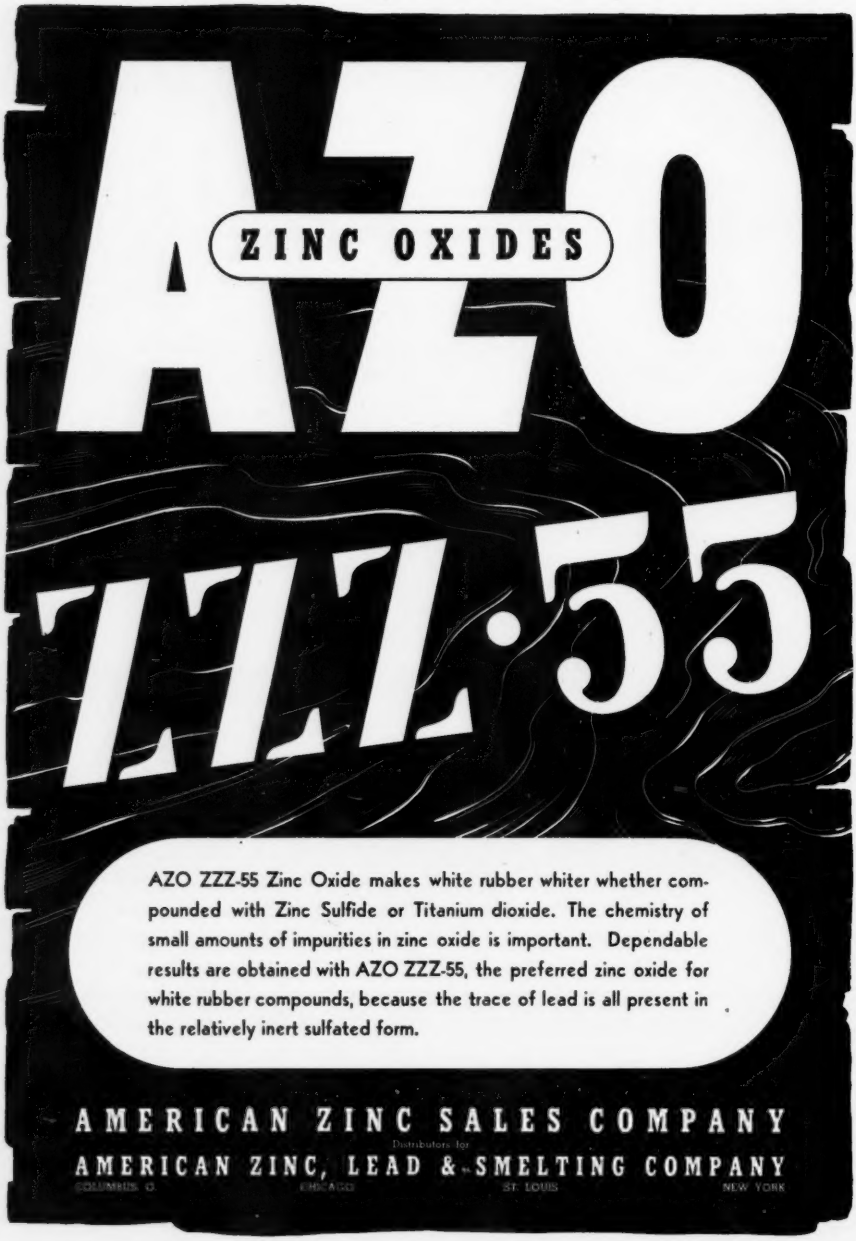
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AZO ZZZ-55 Zinc Oxide makes white rubber whiter whether compounded with Zinc Sulfide or Titanium dioxide. The chemistry of small amounts of impurities in zinc oxide is important. Dependable results are obtained with AZO ZZZ-55, the preferred zinc oxide for white rubber compounds, because the trace of lead is all present in the relatively inert sulfated form.
AMERICAN ZINC SALES COMPANY
Distributors for
AMERICAN ZINC, LEAD & SMELTING COMPANY
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CHICAGO
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Accelerators
• Fluxes •
Antioxidants

A Complete Line of Approved Compounding Materials

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The C. P. Hall Co.

CHEMICAL MANUFACTURERS

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Stamford "NEOPHAX"

Trade Mark Reg. U. S. Pat. Office

VULCANIZED OIL

FOR USE WITH NEOPRENE

The Stamford Rubber Supply Co.

Makers of Stamford Factice Vulcanized Oil

at Stamford, Conn., U. S. A., Since 1900

Factice — The Stamford Rubber Supply Co. — Vulcanized Oil

Short and to the Point

Ask any consumer of St. Joe lead-free Zinc Oxides—or any score of them—what they think of our products, and they will tell you that the quality of the products and service we give them justifies the orders they give us.

ST. JOSEPH LEAD COMPANY
250 PARK AVENUE, NEW YORK, N. Y.

MADE BY THE LARGEST PRODUCER OF LEAD IN THE UNITED STATES

Don't Black-Out Your Name!

Under present conditions some suppliers to the rubber industry, particularly those working on war contracts, are inclined to overlook the importance of keeping in touch with their former customers through the medium of their trade journals.

Though you may not be in a position today to sell any of your regular products to your regular customers, you should keep them posted on what you are doing and remind them that the products which they found so suitable in the past will be back on the market in the future—just as soon as Herr Schickelgruber & Company are taken care of.

It is apparent that the next war will be the "War of Business Survival," in which you will be fighting to get back the business you relinquished of necessity. Now is the time to start your offensive in that direction. Keep telling your customers through the pages of RUBBER AGE (as some of your competitors are already doing) of your service facilities, of maintaining and economizing on your products, of new developments you are now working on for post-war exploitation. These are just a few of scores of ways you can keep your firm and brand names before your customers by means of advertising. We will be glad to tell you on request what various concerns are doing along these lines.

Above all remember, as the U. S. Department of Commerce points out, that *"Brand names fade out of public consciousness fast if they are not kept alive through advertising."*

The RUBBER AGE

One of the World's Outstanding Rubber Journals

250 West 57th Street, New York

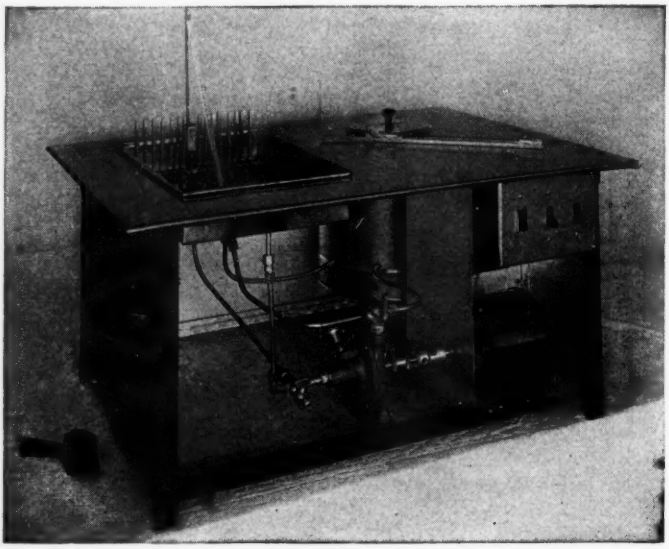
P. S.—Plan now on being represented in the 1943 RUBBER RED BOOK—out in May, 1943.

GET THE MOST FROM YOUR PRODUCT

SCOTT TESTERS*

THE STANDARD OF THE WORLD

For quality production control and for laboratory research of Rubber, Textiles, Wire, etc.



T-50

The Scott line now includes the Naugatuck Chemical apparatus for performing the much-publicized T-50 test.

HENRY L. SCOTT CO.

PROVIDENCE, R. I., U. S. A.

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Justifies its use
always for
COMPOUNDING
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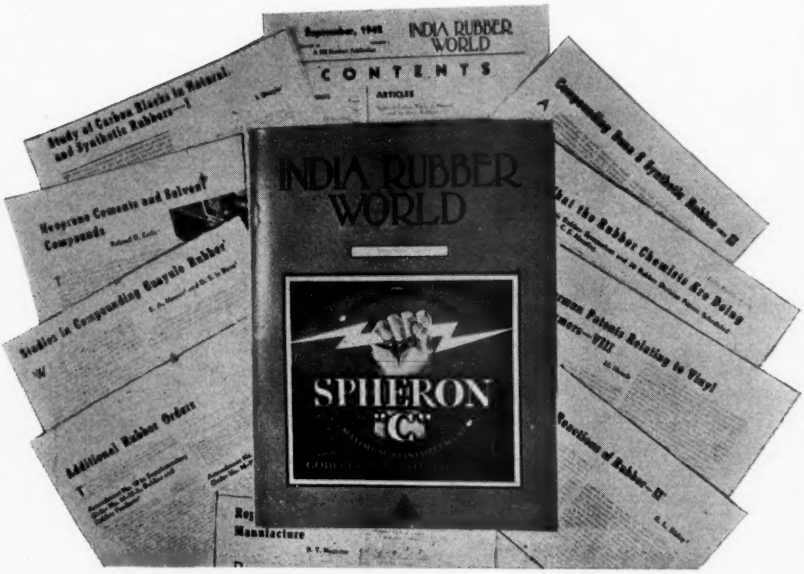

From front cover to back, each issue of INDIA RUBBER WORLD is replete with information regarding the general rubber situation, new compounding practices and ingredients, new materials, new equipment, new Government orders and specifications, the knowledge of all of which is essential to the rubber man who expects to stay in the business.

The recognized authority of the industry, INDIA RUBBER WORLD is a *must* in the library of the rubber man today.

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(Vulcanized Vegetable Oils)

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THE CARTER BELL MFG. CO.

SPRINGFIELD NEW JERSEY

CALCENE

MAKES RUBBER GO FARTHER

Calcene is a re-inforcing Calcium Carbonate pigment of extremely fine particle size. For eight years it has proved its value in making a limited quantity of rubber go farther.

Calcene assures highly loaded stock of low volume cost but with excellent resistance to tear, abrasion and flex cracking.

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PLATE GLASS COMPANY
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New York Cincinnati Cleveland
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GASTEX AND PELLETEX QUARTERLY SUMMARY

Vol. 6 OCTOBER 1942 No. 4

IMPORTANT NOTICE

On October 1, 1942 our New York office was discontinued and our activities transferred to our plant at Pampa, Texas.

This step was taken to conserve time and increase efficiency in the manufacture and distribution of GASTEX and PELLETEX Reenforcing Blacks.

All technical and sales inquiries should be addressed to our general sales agents

HERRON & MEYER

Ohio Building Akron, Ohio

The producers of GASTEX and PELLETEX believe this new move for greater unity of effort will insure still better service for and closer co-operation with our many customers old and new.

Earl J. Wright

Vice President and General Manager

HERRON & MEYER

OHIO BLDG., AKRON, OHIO.

GENERAL SALES AGENTS FOR

GENERAL ATLAS CARBON DIVISION

OF GENERAL PROPERTIES COMPANY, INC.

PAMPA, TEXAS — GUYMON, OKLA.

GASTEX TRADE MARK PELLETEX TRADE MARK

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HERRON & MEYER, New York - Chicago

THE C. P. HALL CO. OF CALIF., Los Angeles ST. LAWRENCE CHEMICAL CO., LTD., Toronto - Montreal

To the
Rubber Industry! ~ ~ ~

This Journal is supported by advertising from leading suppliers to the industry. More advertising will permit the publication of a greater number of important technical papers on rubber which will make RUBBER CHEMISTRY AND TECHNOLOGY even more valuable as a convenient reference of "Rubberana."

Specify materials from suppliers listed on page 27. Urge other suppliers to advertise in

RUBBER CHEMISTRY AND TECHNOLOGY

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Advertising rates and information about available locations may be obtained from S. G. Byam, Advertising Manager, Rubber Chemistry and Technology, care of Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

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A UNIT OF AMERICAN CYANAMID COMPANY

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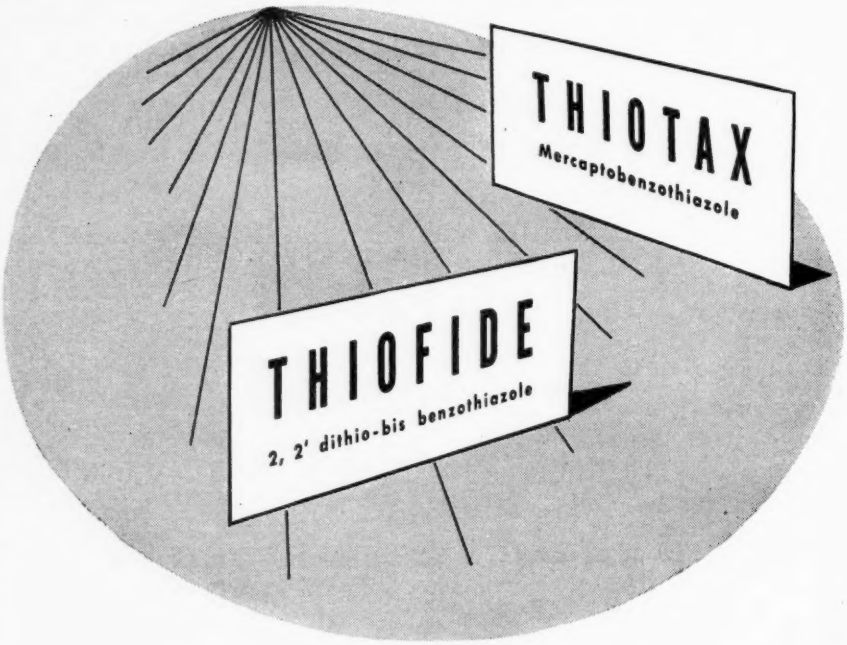
REPRESENTATIVES OF CIA HULERA DE PARRAS, S. A., MEXICO, PRODUCER

Announcing

TWO NEW MONSANTO ACCELERATORS



PROMPT deliveries can be made on these two useful new additions to Monsanto's line of "mercaptos," which already includes SANTOCURE, A-46, EL-SIXTY, UREKA, UREKA-C, and UREKA BLEND B. For samples and experienced technical advice on adapting these accelerators to your needs, inquire: MONSANTO CHEMICAL COMPANY, Rubber Service Department, Akron, Ohio.

MONSANTO CHEMICALS
SERVING INDUSTRY...WHICH SERVES MANKIND

"E" FOR EXCELLENCE—The joint Army-Navy "E" burgee, "representing recognition by both the Army and the Navy of especially meritorious production of war materials," has been awarded to Monsanto and now replaces the Navy "E" first awarded Monsanto December 31, 1941.

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Regular Grades *for* Attractive Color

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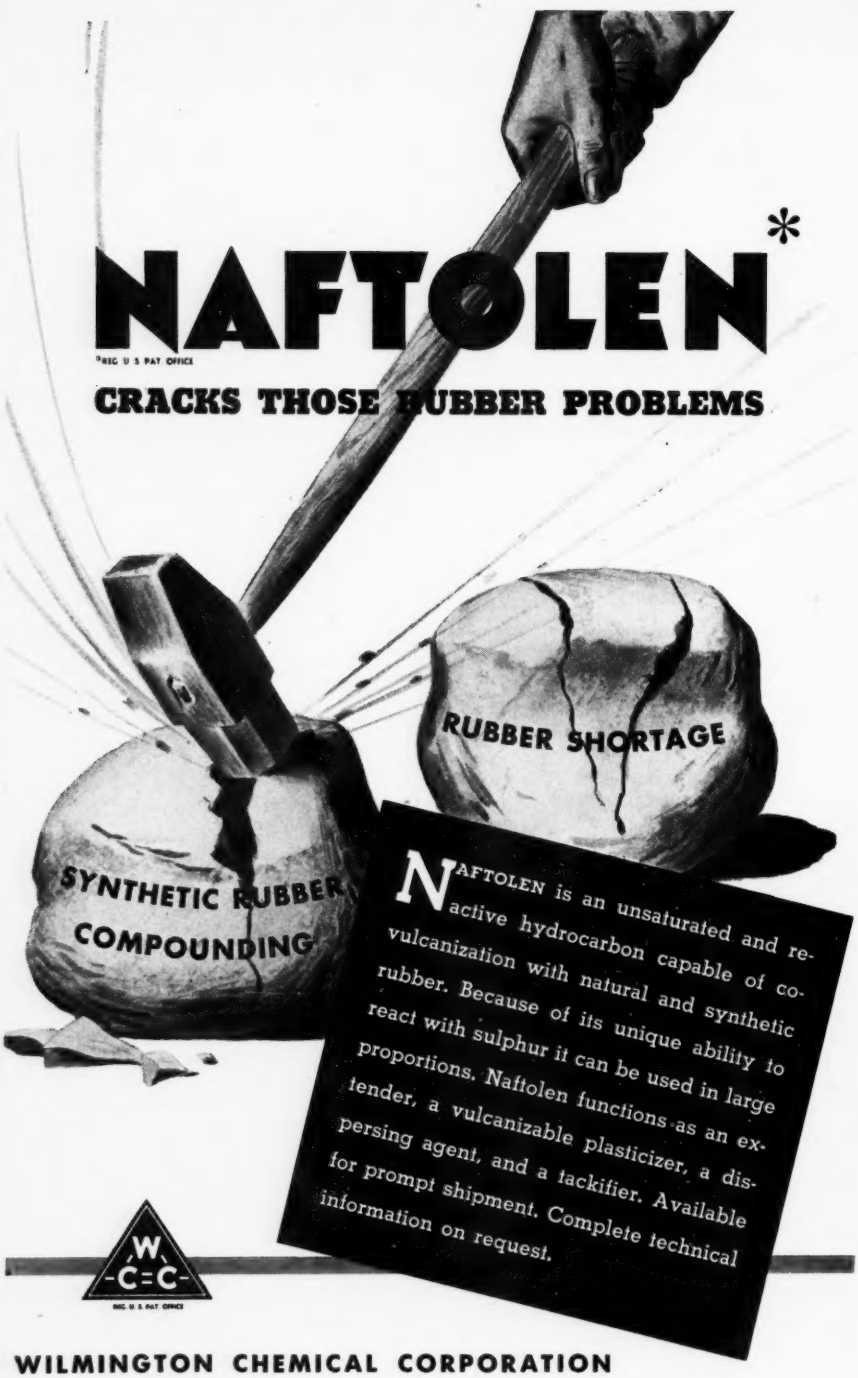
NAFTOLEN*

*REG U S PAT OFFICE

CRACKS THOSE RUBBER PROBLEMS



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